

# THE CAMBRIAN MANGANESE DEPOSITS OF CONCEPTION AND TRINITY BAYS, NEWFOUNDLAND.

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## CONTENTS.

	PAGE.
I. INTRODUCTION .....	371
II. GENERAL GEOGRAPHIC AND GEOLOGIC RELATIONS OF THE MANGANESE DEPOSITS OF SOUTHEASTERN NEWFOUNDLAND .....	373
III. GENERAL STRATIGRAPHY OF DEPOSITS .....	375
IV. DETAILED DESCRIPTIONS OF LOCALITIES .....	377
MANUELS, CONCEPTION BAY .....	377
TOPSAIL, CONCEPTION BAY .....	409
LONG POND, CONCEPTION BAY .....	418
CHAPEL COVE, CONCEPTION BAY .....	419
BRIGUS, CONCEPTION BAY .....	424
SMITH POINT, TRINITY BAY .....	426
V. OTHER MANGANESE DEPOSITS OF SOMEWHAT SIMILAR CHARACTER..	432
PLACENTIA BAY, NEWFOUNDLAND .....	432
MERIONETHSHIRE, WALES .....	433
BATESVILLE, ARKANSAS .....	434
ELBINGERODE, SAXONY .....	435
VI. CHEMISTRY OF THE MANGANESE DEPOSITS .....	437
VII. GENESIS OF THE MANGANESE DEPOSITS AND ASSOCIATED MINERALS..	441
VIII. BIBLIOGRAPHY .....	454

## I. INTRODUCTION.

This paper is based upon data collected during the summers of 1912 and 1913. The former season, Mr. A. O. Hayes and Prof. van Ingen of Princeton University, while making a study of the general geology, stratigraphy, and palæontology of the shores of Conception Bay, Newfoundland, in connection with the investigation of the iron ores of Great Bell Island, came upon the manganiferous rocks of the Lower Cambrian exposed at Manuels, Topsail, Brigus, and other places. They were immediately struck by the unusual lithological and mineralogical characteristics and by the excellent state of preservation, particularly at Manuels, of what are undoubtedly primary

bedded deposits. Some collections and notes then taken of these interesting rocks were later placed at the disposal of the writer for further investigation. The following summer of 1913, the writer as a member of the Princeton Newfoundland Expedition undertook a more detailed study of these deposits at the various localities where the manganese had been found the preceding summer, and also of a deposit of the same age on the northern shore of Trinity Bay.

There are so few syngenetic manganese deposits which still retain their primary unaltered characters and are found to occur at the same horizon over such a wide area that a somewhat detailed investigation gave promise of yielding results of value. In this paper therefore there has been an attempt to present as comprehensive a study of the manganese of southeastern Newfoundland as our knowledge of this hitherto but little investigated region will allow.

The subject matter is primarily chemical in its nature and the analyses herewith presented are from samples taken from the principal manganese-bearing beds. Many more analyses however could have been made and in fact many more should be made if the deposits are to be seriously investigated for commercial purposes. The analyses of the manganese beds at Manuels, Topsail, and Smith Point, Newfoundland and those of the imported specimens from Elbingerode, Saxony were made by the writer in the chemical laboratory of the geological department of Princeton University.

Because of the impalpable fineness of grain of many of the manganese-bearing beds, the petrographical descriptions of certain of the thin sections can deal only with the larger features such as structure, mineral aggregations, and a few of the larger and observable minerals.

The writer feels particularly indebted to Prof. C. H. Smyth, Jr., for many helpful suggestions bearing upon the chemical side of the investigation, and to Prof. G. van Ingen for unpublished information regarding the stratigraphy and palæontology of this region, as well as for the loan of the locality maps and data for the columnar sections which are the results of careful surveys made during the summers of 1912 and 1913. All photographs and microphotographs were generously contributed by Prof. van Ingen to further the presentation of the results of this investigation.



## II. GENERAL GEOGRAPHIC AND GEOLOGIC RELATIONS OF THE MANGANESE DEPOSITS OF SOUTHEASTERN NEWFOUNDLAND.

### GEOGRAPHIC RELATIONS.

The manganese deposits here considered are located in the south-eastern part of Newfoundland in the vicinity of Topsail, Manuels, Long Pond, Chapel Cove, and Brigus on Conception Bay, and at Smith Point on Trinity Bay. Manganese is also said to occur near Ships Cove, Placentia Bay. The accompanying map, Fig. 1, shows the approximate location of these deposits.

### GENERAL GEOLOGY.

The sedimentary rocks of this area are included in the Cambrian and Ordovician systems and may be seen on the map (Fig. 1) to occur as irregular patches, the Ordovician composing the larger islands of the bays and the Cambrian occurring as irregular and widely separated fringes resting on the pre-Cambrian of the mainland. The whole series consists almost wholly of shales and thin-bedded sandstones with some limestones, and in the base of the lower Cambrian an occasional conglomeratic bed.

The iron ores of Great Bell Island are Arenig while the manganese and their associated green and red shales are of late lower Cambrian.

Wherever the Cambrian strata have been found in contact with the pre-Cambrian an unconformable relationship exists. The pre-Cambrian rocks of this area as classified by Dr. Walcott (2:219) and by Messrs. Murray and Howley (18:141-154) respectively are as follows:

	Walcott	Murray and Howley
	Random	
Avalonian	{ Signal Hill	Avalonian
	{ Momable	
	{ Torbay	
	{ Conception	Huronian
	{ Laurentian	Archaean

The Avalonian and Huronian of Mr. Howley represent a thickness of 12,370 feet. A later unpublished estimate of 18,250 feet has

been made by Mr. A. F. Buddington, who is studying the pre-Cambrian rocks of this region. A brief description of these formations at this time will be necessary for a comprehensive view of the Newfoundland manganese deposits.

*Laurentian:* The rocks of this formation are in great part gneissic and granitoid, and are probably the oldest rocks of the area.

*Huronian:* This formation, which is equivalent to the "Conception" of Dr. Walcott, consists principally of the Conception slates which are of tufaceous marine origin. They are intruded by bosses and dikes of granite, diorite, monzonite, and gabbro, and contain basaltic and rhyolite flows. The Conception formation was estimated by Murray and Howley to have a thickness of 2,950 feet.

*Torbay:* This formation consists of about 3,300 feet of green and purple slates and argillites.

*Momable:* An estimated thickness of 2,000 feet of brown and black sandy shales overlies the previous formation.

*Signal Hill:* Red and green sandstones, conglomerates, shales, and arkoses largely of continental origin comprise this formation, the thickness of which is about 9,000 feet according to an unpublished estimate by Mr. A. F. Buddington.

*Random:* About 1,000 feet of green and red sandstones and white quartzites with occasional basalt flows comprise this series.

Murray and Howley in their report of 1868 for the Geological Survey of Newfoundland describe the general structural features of the Avalon Peninsula as follows:

"The region in question, in particular, and probably the whole island in general, seems to be arranged in an alternation of anticlinal and synclinal lines, independent of innumerable minor folds, which preserve throughout a remarkable degree of parallelism, pointing generally about N-NE and S-SW from the true meridian, corresponding with the strongly marked indentations of the coast as well as the topographical features of the interior. One such great anticlinal form occurs within the region examined this year, with a corresponding synclinal; the axis of the former was found to be more or less overlaid unconformably by rocks containing fossils of Lower Silurian age, none of which were of less remote antiquity than such as are attributed to the horizon of the upper Potsdam group."

"The axis of this anticlinal runs in a moderately straight line from Cape Pine on the south coast to that part of the Peninsula and coming up from below the Intermediate Series, occupies more or less of the surface from the vicinity of the Renew's Butterpots to the shores of Conception Bay be-

tween Holyrood and Manuels Brook. The newer or Great Intermediate Series which flanks this Laurentian Nucleus, was found on the Peninsula of St. Johns and Ferryland to show a general dip to the eastward although making many minor undulations; while on the Peninsula between Conception and Trinity bays the inclination is reversed, being nearly uniformly westerly, making many repetitions of the same strata however, as on the opposite side of the fold. Corresponding with this great anticlinal, the measure of the Intermediate rocks, as seen at parts of the eastern coast of Placentia Bay, appear, by the generally eastern dip which they present, to indicate the axis of a synclinal trough to run from Trinity Bay in the direction of St. Mary's Bay."

As structural work of a reconnaissance nature only has thus far been published in reference to Newfoundland it is hoped that this most interesting phase of geology of the island may be investigated in the near future. The following locality descriptions will take up briefly these smaller structural features which may serve as a clue to the more general structures of the entire manganese area.

### III. GENERAL STRATIGRAPHY

There is very little published information regarding the general stratigraphy of the region under consideration but a few observations made while studying the individual manganese deposits and other information verbally communicated by Prof. van Ingen may be of interest at this point.

One of the most striking features of the manganese deposits is their occurrence at the same horizon in shales of late lower Cambrian age at widely separated points on Conception and Trinity Bays. At each deposit, the manganese zone was found to occur below the Paradoxides zone. At Manuels in the shales directly below the manganese nodular beds, heads of *Protolenus harveyi* (oral communication by G. van Ingen) were found so that in all probability the manganese beds may be included in the *Protolenus* zone of Matthews (16: 101-153).

By referring to the columnar sections (Figs. 2, 36, 42, and 44) it is readily seen that the sediments consist largely of shales and limestones and that there is a very decided increase in the total thickness of the beds from Manuels where there are 215 feet between the bottom of the Paradoxides zone and the top of the pre-Cambrian to Smith Point, Trinity Bay, where over 1,000 feet intervene between

the Paradoxides zone and the pre-Cambrian. From the bottom of the Paradoxides zone at Smith Point to the top of the Smith Point limestone according to a calculation based upon a careful stadia transit survey of the shore line (Fig. 43) there is a thickness of 546 feet. The total thickness in the number of limestone beds varies from a few feet at Manuels to 100 + feet at Smith Point. The thickness of the shales at Manuels below the Paradoxides zone is about 200 feet while the thickness of the shales at Smith Point within the corresponding limits is over 400 feet, on the assumption that the Smith Point limestone of Trinity Bay corresponds to that limestone of the Manuels section which is just above the basal conglomerate.

The increase in total thickness of the number of beds from the east shore of Conception Bay to the west shore within the corresponding limits would indicate a deeper portion of the Cambrian sea when the sediments were being deposited. The fact that sediments found below the Smith Point limestone on Trinity Bay are not represented at Manuels would indicate that sedimentation had been going on for a longer time in the western portion of the basin than in the eastern. Whether there actually was a greater amount of sedimentation in that portion of the basin remains to be investigated.

As very little information is at hand with regard to the area of the Cambrian rocks, it is quite out of the question for the writer to attempt to outline the area once occupied by the Cambrian Sea in southeastern Newfoundland. Moreover, it is likewise impossible for the writer to outline the original manganese area as it looked in early Cambrian times. If manganese occurs on the eastern shore of Placentia Bay, as all descriptions of that occurrence seem to indicate, it would seem that the original area of the manganese was approximately 200 or 300 square miles, assuming a more or less oblong shape for the deposit.

Although the basal conglomerate at Manuels is evidence of a definite shore line for the Cambrian sea at that part of the basin, there is also evidence at the other localities examined, where, however, the basal conglomerate is not found in any such large development. There are littoral pre-Cambrian contacts at Topsail, Chapel Cove, and Brigus; all with typical shore deposits.

## IV. DETAILED DESCRIPTIONS OF LOCALITIES

MANUELS.—Manganese is found as thin jasper-like bands of green and brown color, as nodular beds, and as argillaceous and calcareous beds interbedded with green and red shales of late lower Cambrian age. This mode of occurrence is very well shown in Manuels brook close by the village of Manuels. The geographic, geologic, and stratigraphic relations are shown in Figs. 1-3. The Cambrian at Manuels consists in the main of shales with thin bedded sandstones with conglomerate and thin limestones at its base and the sediments show practically no metamorphism throughout the series. The strike of the beds is N 82 E (true meridian) and the dip is 10 N. One of the best unconformable contacts in the manganese area is that in Manuels brook at Manuels where the basal Cambrian conglomerate lies upon the Huronian. For a more intimate acquaintance with the manganese occurrence a somewhat detailed description of the stratigraphy, lithology, mineralogy and petrography of the manganese beds and their associated strata will be necessary and therefore the individual beds of the section (Fig. 2) will be described in stratigraphical order.

**210 A 1**, Basal Conglomerate. The base of the Cambrian at Manuels is made up of coarse conglomerate, eighteen feet in thickness, consisting in the main of boulders and pebbles of igneous character. These boulders at the bottom of the bed, where the base of the Cambrian lies unconformably upon the Huronian, measure in some instances twelve feet in diameter, but they diminish in size toward the top to an inch or less. The matrix, of an arenaceous nature toward the bottom, grades into a more calcareous one at the top where the overlying stratum is a limestone.

**219 D 1**, limestone. This bed is a bluish fine-grained to pebbly argillaceous limestone of about 3 feet in thickness. The pebbles averaging a fraction of an inch in diameter are angular to subangular in shape and appear to be of igneous rocks. Pteropod shells chiefly of the genus *Coleoloides* abound. Microscopic examination proves this rock to be a semi-crystalline, fine to locally coarse grained limestone. The texture is very suggestive of organic forms, being an aggregate of elliptical bodies, possibly algal concretions [or "copro-



## Manuels River

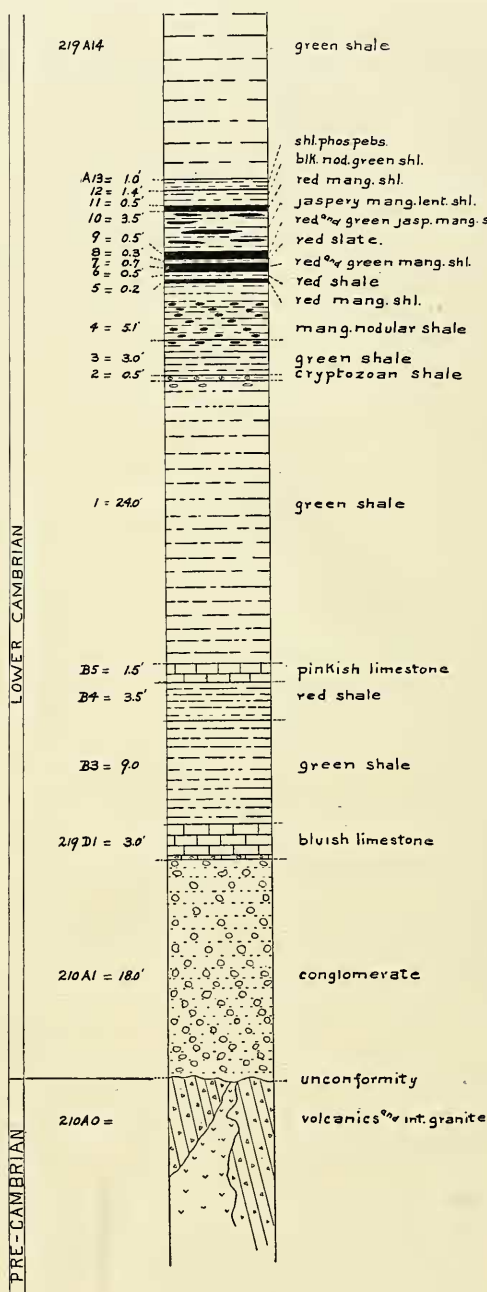


FIG. 2. Columnar section showing the details of the manganese zone in the Lower Cambrian of Manuels brook, 219 A and B.

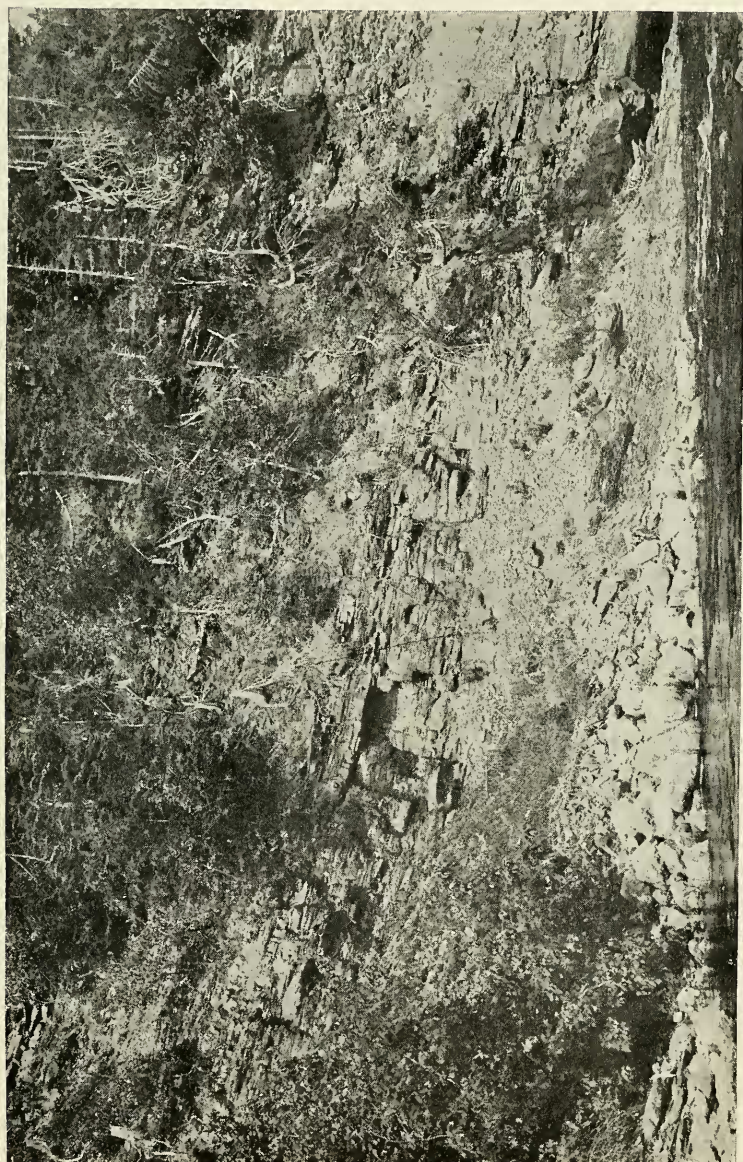


FIG. 3. View of outcrop of manganese zone of late lower Cambrian age in left bank of Manuels brook.

lite ooze" similar to that described by Philippi from off the Congo mouths—G. van Ingen]. These bodies contain aggregations of carbonate material, probably calcite, which have no definite orientation. The section abounds with pteropod shell fragments, partially replaced with calcite. Calcite and carbonate material comprise the greater portion of the section but quartz occurs as infrequent local segregations and as irregular grains. Pyrite and hematite, as well as a few pink and brown stained areas which are possibly secondary products of manganese and iron, are sparingly present. No analysis was made of this rock but with the sodium carbonate and potassium nitrate bead test a manganese reaction was obtained. This bed is a bluish argillaceous manganiferous limestone.

**219 B 3**, overlying the limestone, is a brownish weathering olive green shale.

**219 B 4** is a bed of red shale, the upper surface of which seems to be limy. The upper 2 inches of this bed has a wavy structure and is somewhat greenish in color. Microscopically the bed is found to be a hematitic shale with occasional grains of quartz and thin rectangular laths of feldspar. Magnetite and pyrite are found as irregular grains in sparing amounts.

**219 B 5**. With a sharp contact, the red shale is overlain by a 1.5 foot thick bed of nodular and pebbly reddish blue limestone. Because of marked lithological differences this bed has been divided into four smaller subdivisions which are lettered **a**, **b**, **c**, and **d**. Subdivision **a** consists of about 2 inches of green shale which is slightly calcareous. Subdivision **b** is a compact pinkish limestone containing pinkish or reddish mineral disseminations and occasional fragments of hyolithid and brachiopod shells. Microscopically this limestone is somewhat granular and crystalline, with calcite as the dominant anisotropic mineral. Quartz occurs occasionally. Hematite as an impalpable dust or pigment is abundant, bordering hyolithid fragments or as irregular accumulations. A fragment of probably organic substance with a cellular structure is a conspicuous feature of the slide. Sponge spicules replaced by calcite are noticeable.

Subdivision **c** differs not very much from the two members described but is nodular or pebbly and much more fossiliferous. Micro-



scopically this rock is a very fine grained semi-crystalline limestone. Calcite, frequently twinned, is the dominant mineral with quartz and chlorite in secondary importance. Barite occurs as occasional small and large irregular grains. Hematite is found bordering calcite grains and fossil fragments or replacing them, and as irregular accumulations. Pyrite is found occasionally. Certain nodular or pebbly forms, isotropic under crossed nicols, are, because of their fineness of grain, of an indeterminable nature.

A very noticeable feature of this section is the diversity of *Hyolithes* forms, some elliptical and concentric and others circular, either entirely or partially replaced by calcite or hematite. The circular forms measure .287 mm. in diameter (Fig. 4, Slide 250).

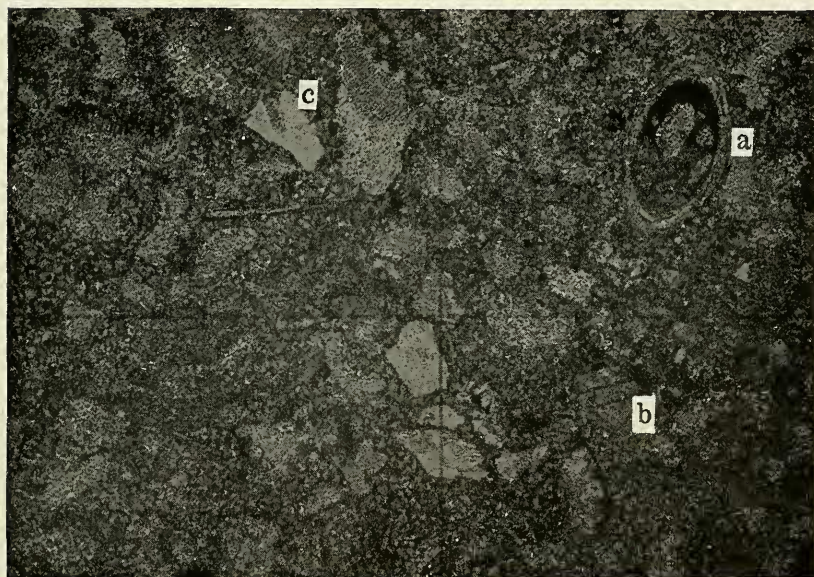


FIG. 4. Microphotograph of limestone, 219 B5c; slide 250; enlarged 22 diam. a, hyolithes with calcite and chlorite; b, calcite; c, quartz.

**219 B 5d.** The upper subdivision of this bed is of interest mainly on account of the mineral associations in the large nodules on its surface. Differential erosional effects between the limestone and nodule have resulted in a greater conspicuousness of the more resis-

tant nodule. The nodules, measuring as much as 6 inches in diameter, consist largely of argillaceous material, jaspery concentric bands, blades of barite, pyrite and some disseminated manganiferous and ferruginous carbonate minerals which are surrounded by dark areas. These latter are probably manganese oxide zones due to the alteration of a manganiferous carbonate.

Under magnification these nodular portions are roughly concentric and laminated in structure, with laminations red and green in color, and of fine and coarse grain. An oölitic structure, but with the spherules poorly formed, is found in combination with the banded structure. Calcite occurs as somewhat elongated crystals and is the dominant mineral. Wherever the calcite presents the peculiar elliptical and circular shapes mentioned on page —, an organic origin is immediately suggested (Fig. 5 and 6, Slide 254).

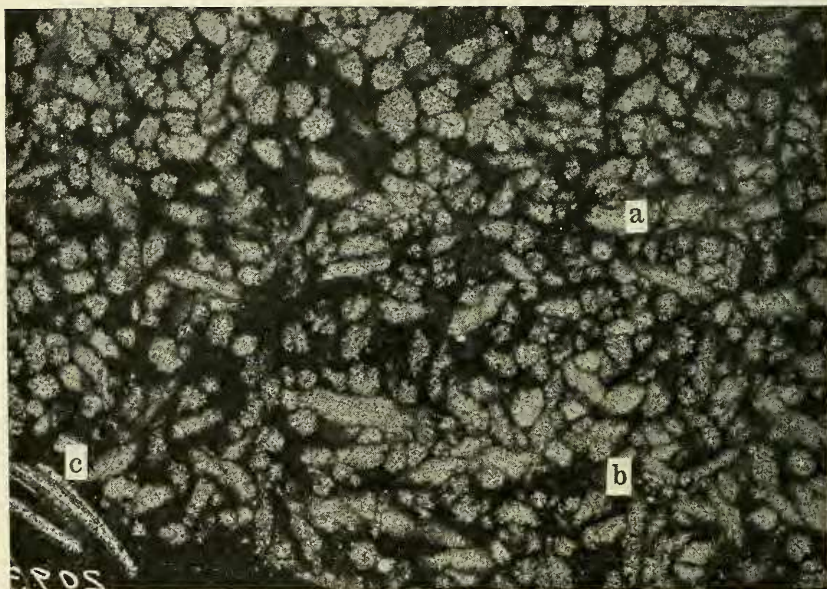


FIG. 5. Microphotograph of limestone, 219 B5d; slide 254; enlarged 22 diam. a, elliptical calcite aggregations; b, chlorite; c, hyolithes.

Quartz is found as irregular grains and aggregations. Barite occurs only sparingly. Among the opaque minerals, pyrite sometimes alter-



ing to limonite, is most conspicuous and occurs as large irregular grains and areas surrounding fossil fragments and associated with



FIG. 6. Microphotograph of limestone, 219 B5d; slide 254; enlarged 22 diam. a, calcite; b, quartz; c, phosphatic? nodules.

more calcareous portions. Hematite (Fig. 7, Slide 257) is found in the more jaspery or laminated areas as irregular grains, aggregations, and spherules associated particularly with the green area which for the most part is of an indeterminable character. Veins of calcite are found cutting the nodule. As in the layer above, there are found in this one (Fig. 8, Slide 253), certain semi-isotropic nodular areas or pebbles which are partially chloritized. It is very possible that these nodular or pebbly areas are similar to the phosphatic nodules of 219 A 13 to be described later. These alter to carbonate locally. Among the organic remains are fragments of shells, hyolithes, trilobites, and sponge spicules, which in part show carbonate and chloritic replacement (Fig. 5, Slide 254, and Fig. 7, Slide 257).

**219 A 1.** Disconformably upon the above described nodular limestone there rests about 34 feet of a hard, fissile, green shale. About



FIG. 7. Microphotograph of sponge spicules, 219 B6a; slide 257; enlarged 22 diam. a, sponge spicule; b, hematite; c, calcite.

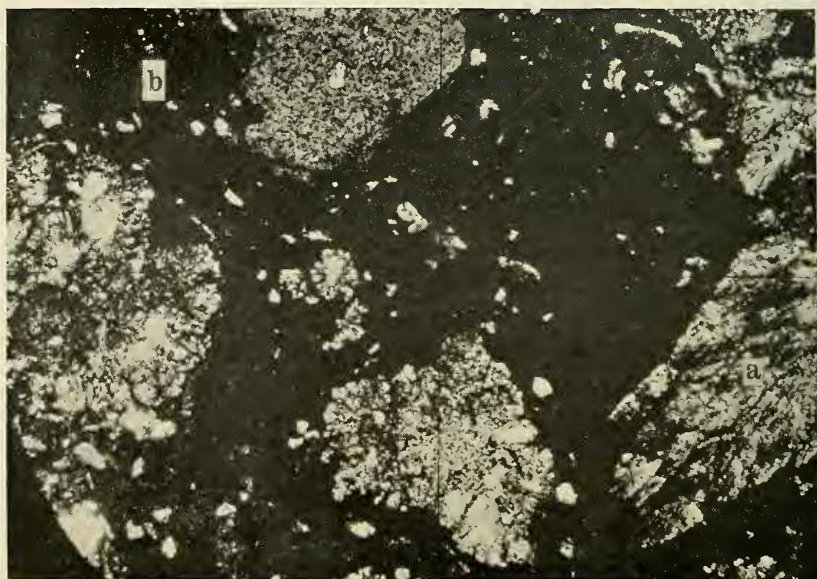


FIG. 8. Microphotograph of limestone, 219 B5d; slide 253; enlarged 22 diam. a, calcite; b, phosphatic? material.

5 feet above the limestone there are thin seams full of comminuted fragments of small *Lingulella*, and *Hyolithes* shells. The upper part of this shale is conspicuous because of the conchoidal fracture with which it breaks and the presence of local aggregations of small subspherical black nodules some of which show pinkish centers of some fine-grained minerals such as rhodochrosite or manganiferous calcite.  $\text{MnO}_2$  occurs as small dots or as dendritic areas on the fracture planes. Microscopically, this is a chloritic micaceous shale containing sparingly, among the visible minerals, irregular grains of plagioclase, quartz, pyrite, magnetite and limonite in descending order of abundance.

**219 A 2** is a nodular shale bed of .5 of a foot in thickness and forming the sloping surface over which the stream runs. This bed is noteworthy because of the *Cryptozoon* colonies showing on the surface (see Fig. 10).

**219 A 2a**, the lower portion of this bed, is a green shale containing frequent small subspherical nodules and disseminations of a pink carbonate which effervesces freely and is in all probability a manganiferous calcite similar to the pink nodules analyzed (see page 395).

**219 A 2b** is the *Cryptozoon* shale bed and contains roughly concentric or zonal structures measuring  $1\frac{1}{2}$  inches in diameter, irregular and sub-spherical nodules measuring 1 inch in diameter, and intercalated lenses of manganiferous calcite. These nodular and *Cryptozoon* structures weather brown. Scattered through the bed, particularly the shaly portions, are blades of barite.

Microscopic examination of this *Cryptozoon* bed brings out nothing which can be said to be of an organic structure. What structure there is may be characterized as broken veinous, concentric and laminated. The texture in great part is crystalline. The greater portion of one of the nodules consists of calcite and carbonate. Barite occurring as long blades is determined principally by the two cleavages, c and m, its birefringence greater than quartz and its biaxial + character. Chlorite either alone or in combination with carbonate is found replacing barite. Calcite or carbonate occur as irregular masses or as rudely formed or incipient spherules. Hematite occurs in the banded portions as more or less massive bands interlaminated with chlorite or as rudely formed spherules in the





FIG. 9. Details of lower portion of manganese zone in Manuels brook.

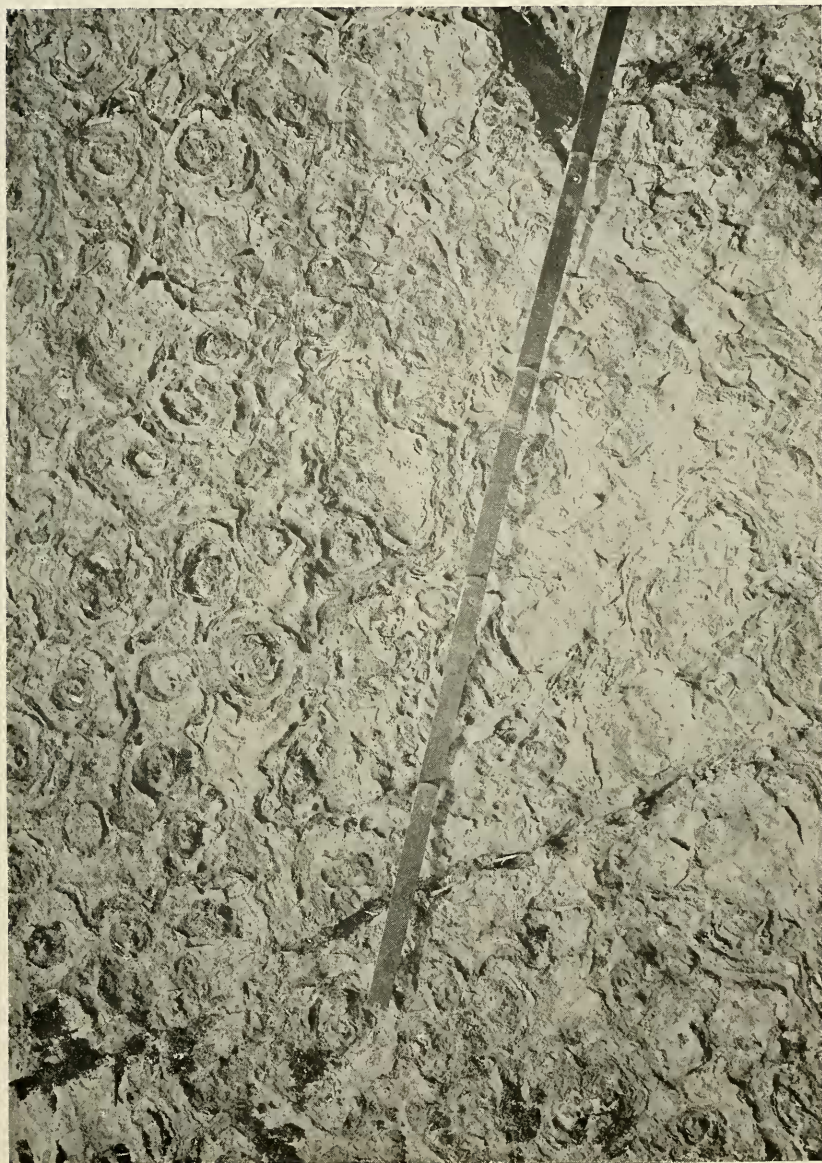


FIG. 10. Photograph of upper surface of Cryptozoon bed, 219 A2, in left bank Manuels brook.





FIG. 11. Microphotograph of section of *Cryptozoon* nodule, 219 A2; slide 292; enlarged 22 diam. a, ferruginous band; b, calcite.



FIG. 12. Microphotograph of *Cryptozoon* nodules from 219 A2, showing barite being replaced by chlorite; slide 292; enlarged 22 diam. a, barite; b, chlorite; c, ferruginous and calcareous shale.

ground mass. These spherules measure as small as 9 microns in diameter but have an average diameter of between 30 and 40 microns (Fig. 11 and 12, Slide 292).



FIG. 13. Middle portion of manganese zone in Manuels brook. The numbers are those of the section.



The paragenesis of minerals within the nodules is as follows: Calcareous or carbonate material with probably synchronously formed hematite, barite veining, chloritization replacement, and finally calcite as vein or replacement material.

**219 A 3** is a green shale bed, 3 feet in thickness, lying conformably above the *Cryptozoon* nodular bed. For the most part this bed consists of a hard fissile green shale which breaks with a conspicuous

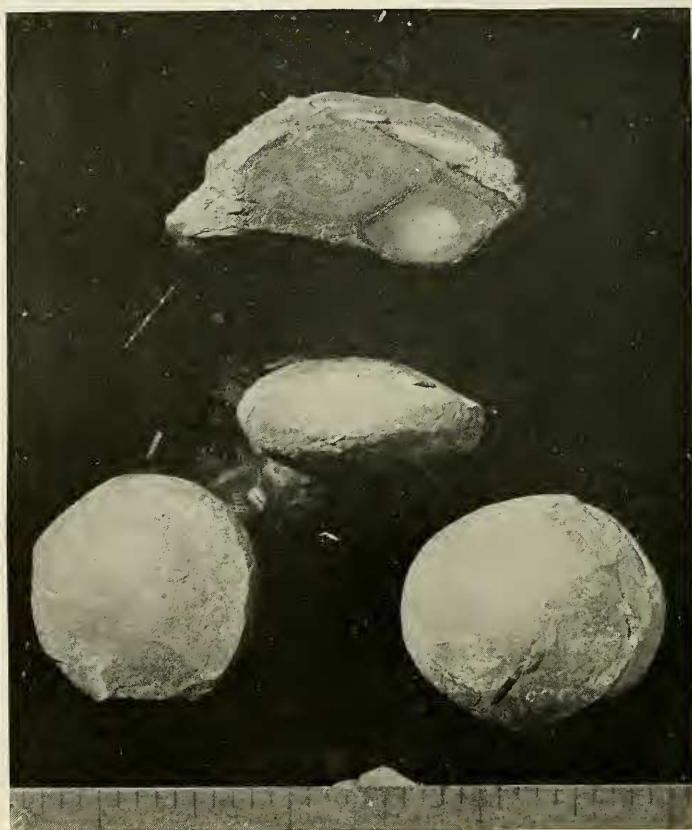


FIG. 14. Photograph of manganese carbonate nodules extracted from shale 219 A4, natural size. Top, side and sectional views.

conchoidal fracture. 3 inches above the *Cryptozoon* bed is a layer containing fragments of trilobites which according to Prof. G. van Ingen are probably to be identified as *Protolenus harveyi*. Barren

green shale overlies this fossiliferous layer and this in turn is followed by nodular green shale containing manganiferous calcite nodules, a description of which is given in connection with the following bed.



FIG. 15. Photograph, natural size of ground and polished horizontal section of shale containing manganese carbonate nodules from 219 A4.

**219 A 4** is a conspicuous rhodochrosite and manganiferous calcite nodular bed and may be considered the base of the manganese zone at Manuels (Fig. 13). Structurally this is a nodular and oölitic bed, the former structure conspicuously observable macroscopically, and the latter, though not so well defined a structure, observable microscopically. The entire bed measures 5.1 feet in thickness and is divisible into two members, **a** and **b**. The lower member, **219 A 4a** is a predominantly nodular reddish green shale while the upper division or **b** member is not so nodular.

The nodules of 219 A 4a are discoidal in shape and vary in diameter from  $\frac{1}{6}$  inch to  $1\frac{1}{2}$  inch, with an average of about 1 inch and a thickness ranging from  $\frac{1}{8}$  inch to  $\frac{1}{2}$  inch. The longer diameters of the nodules lie in the plane of the bed. Where the nodules are very numerous or crowded they are found intergrown with or overlapping each other. Specimens ground and polished often show a lenticulate formed by two nodules (Figs. 14 and 15). In color they are for the most part green, but may have greenish, white, or pink central cores. Cross sections of the nodules reveal a distinct zonal arrangement with spherical central cores surrounded by concentric

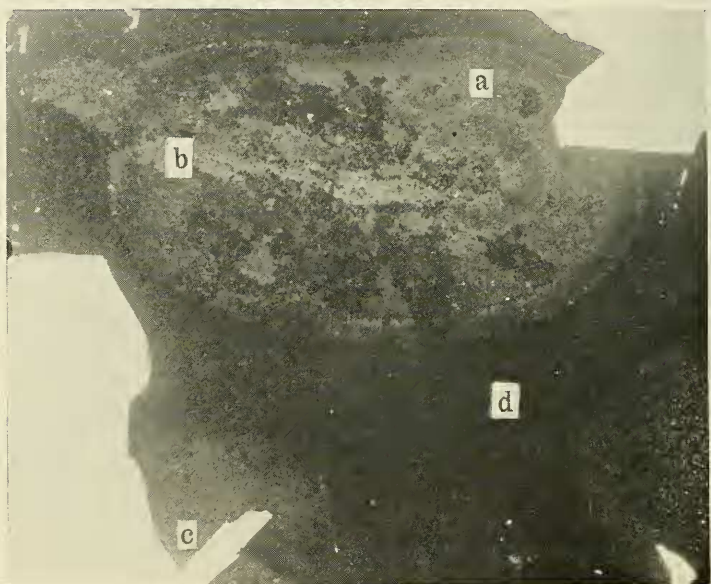


FIG. 16. Microphotograph of manganese carbonate nodule from 219 A4a; slide 288; enlarged 6 diam. a, carbonate of manganese, lime and magnesia; b, barite; c, barite replaced by chlorite; d, shale.

shells conforming to the shape of the nodule. The grain of the nodules is usually exceedingly fine, impalpable or crystalline. The pinkish cores are usually crystalline and respond to the HCl test quite readily, indicating some carbonate mineral. By analysis the green nodules are found to consist essentially of rhodochrosite (see Anal. B, page 395), while the pinkish crystalline mineral occupying



the centers of the nodules or occurring as intercalated lenses or nodules in the nodular bed is found to be essentially a maganiferous calcite (see Analysis C, page 395).



FIG. 17. Microphotograph of coalescing nodules from 219 A6c; slide 243; enlarged 4 diam. a, carbonate of manganese, etc.; b, oölitic shale.

Further macroscopical examination of the nodules shows the presence of barite blades within the central portions of the nodules or disseminated throughout the nodule or its shaly matrix. The characteristics which determined the barite are its c and m cleavage, its hardness of 2 and its diaphaneity. Its optical properties confirm it microscopically. Pyrite is found sometimes completely surrounding central cores as irregular and continuous grains. The surfaces of the nodules usually are covered with minute pink or reddish disseminated grains which upon microscopic examination are found to be hematitic spherules.

Thin sections of these nodules, on the whole, are not satisfactory for microscopical work because of the almost impalpable fineness of the grain. However some of the larger features may be of interest and importance. The structure is nodular and concentric and some of the concentric shells are oölitic. In all the thin sections of nodules the most conspicuous feature is the zonal arrangement of crystalline and indeterminable portions. The crystalline parts usually occupy the centers of the nodules while the impalpable or indeterminable areas are arranged around the centers (see Fig. 16, Slide 288). However some of the cores consist of indeterminable material. The zones are sometimes marked off from each other by more or less sharp contracts as brought out by a difference in shade of color or by an apparent difference in grain (Figs. 17, and 18).

The exterior zones merge imperceptibly into the shale, a fact which has some genetic significance.

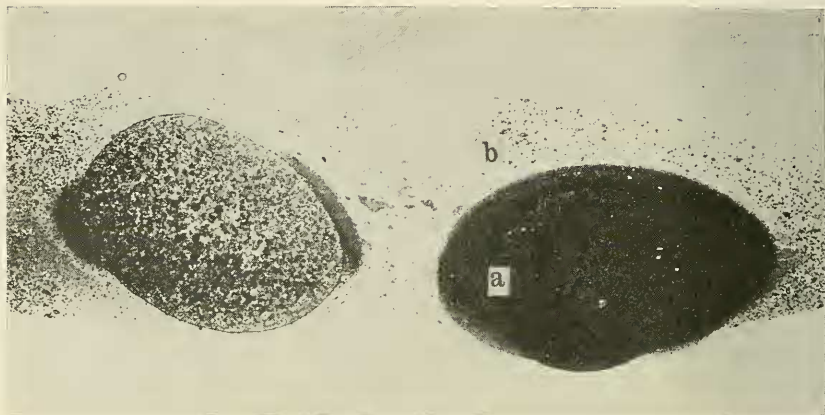


FIG. 18. Microphotograph of two manganese carbonate nodules from 219 A6c; slide 237; enlarged 8 diam.

An incipient oölitic structure with spherules of hematite is common to the outer zones of the nodule and shaly matrix. The spherules do not as a rule show any well-developed zonal structure nor are they of very regular form. They vary in diameter from 6 microns to 77 microns and have an average diameter of about 24 microns. Not infrequently the spherules consist of both carbonate and hematite, the former preserving a radiating structure and abounding in the more calcareous portions of the specimen, while the hematitic spherules are more common in the shaly parts.

Among the determinable minerals are calcite, which occurs as anhedral grains of variable dimensions in small crystalline areas, in veins, or as replacement material after organic remains such as sponge spicules, etc. Carbonate material for the most part specifically indeterminate makes up the greater part of the slide. Barite is found occupying the more central portions of the nodule in some sections. Quartz as irregular grains occurs only in sparing amounts. Pyrite is present as large and small irregular grains and masses.

The analyses of the green and pink nodules are as follows:

ANALYSIS B.		ANALYSIS B 1.	
<i>Green Nodules.</i>		<i>Recalculation.</i>	
SiO <sub>2</sub> .....	10.31	MnCO <sub>3</sub> .....	39.56
Fe <sub>2</sub> O <sub>3</sub> .....	7.35	MnO .....	7.30
Al <sub>2</sub> O <sub>3</sub> .....	3.68	CaCO <sub>3</sub> .....	18.61
MnO .....	31.76	MgCO <sub>3</sub> .....	3.79
CaO .....	10.46	SiO <sub>2</sub> .....	5.94
MgO .....	1.80	BaSO <sub>4</sub> .....	6.29
BaSO <sub>4</sub> .....	6.43	H <sub>2</sub> O .....	1.51
H <sub>2</sub> O .....	2.85	Fe <sub>2</sub> O <sub>3</sub> .....	7.35
CO <sub>2</sub> .....	25.31	2H <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> .....	9.17
	99.96		99.52

ANALYSIS C.		ANALYSIS C 1	
<i>Pink Nodules.</i>		<i>Recalculation.</i>	
SiO <sub>2</sub> .....	5.14	CaCO <sub>3</sub> .....	58.05
Fe <sub>2</sub> O <sub>3</sub> .....	1.40	MnCO <sub>3</sub> .....	29.32
Al <sub>2</sub> O <sub>3</sub> .....	1.64	MnO .....	2.34
MnO .....	20.49	SiO <sub>2</sub> .....	3.78
CaO .....	32.92	Fe <sub>2</sub> O <sub>3</sub> .....	1.40
MgO .....	.01	H <sub>2</sub> O .....	1.06
H <sub>2</sub> O .....	1.65	2H <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> .....	4.07
CO <sub>2</sub> .....	36.77		100.02
	100.02		

The pinkish crystalline mineral which exhibits a rhombohedral cleavage, has a hardness of about 3, effervesces freely with HCl acid, and, with the above composition, is essentially a manganiferous calcite. The excess MnO probably exists as a peroxide of manganese as indicated by the considerable amount of chlorine which was given off while the sample was being digested with HCl acid. As no thin sections were made of this specimen no petrographic confirmations can be made.

The upper subdivision of 219 A 4 (219 A 4b) is a greenish and reddish nodular shale bed measuring 2.9 feet in thickness and divisible into three roughly distinct portions. The lower part, 219 A 4b 1 is a greenish red shale overlaid by a reddish shale with occasional small nodules measuring about ¼ inch in diameter (Fig. 13, and 19).





FIG. 19. Middle and upper portions of manganese zone in Manuels brook.

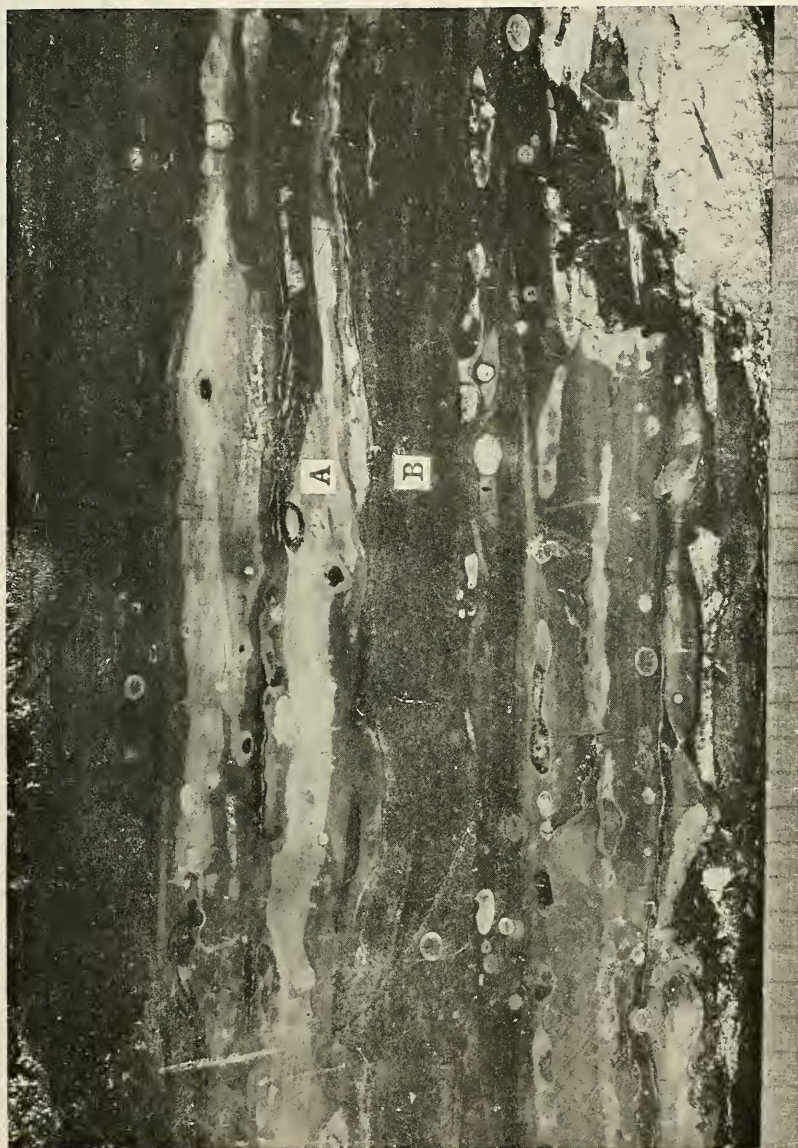


FIG. 20. Photograph of polished vertical section of banded manganese carbonate-oxide ore, 219 A7, slightly enlarged (1.8 diameters). a, green band; b, red band.



Under the microscope a thin section of this bed reveals hematite in the form of a pigment and as grains and ill-formed spherules, while local areas of carbonate are found. The upper member of this bed, **219 A 4b 3** is a red shale containing small subspherical and discoidal nodules quite similar to those described in detail above.

**219 A 5** is a nodular ferruginous shale which is calcareous and manganeseiferous. The shaly structure and the manganese are brought out in a conspicuous way through weathering; the manganese by the black discoloration in evidence as one of the derived oxides. This bed has a thickness of .2 of a foot but thins and thickens, presenting a lenticular appearance. The nodules, or possibly pebbles, are subspherical in form, dark green in color, and of impalpable fineness of grain. They resemble those already described in connection with the

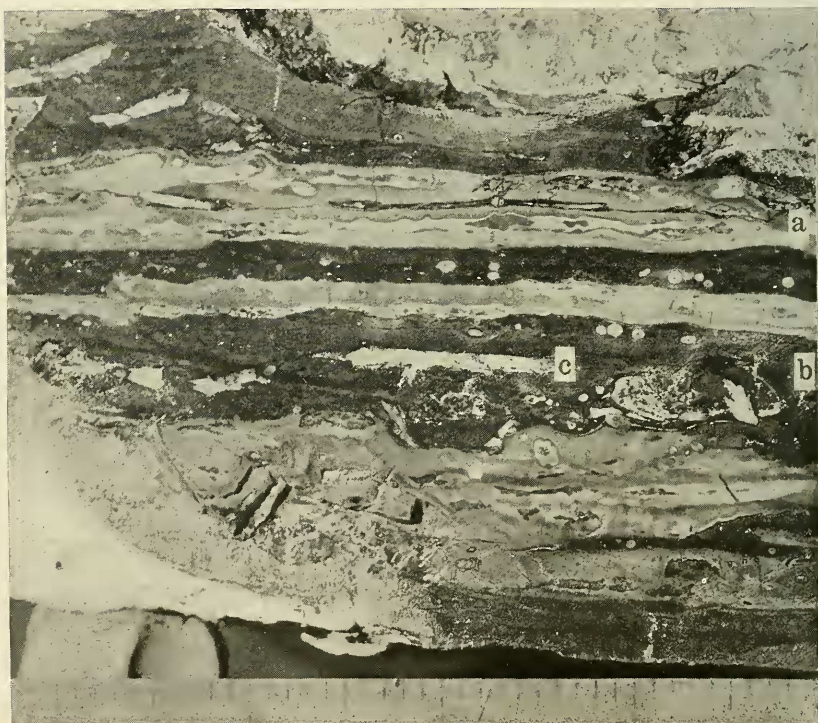


FIG. 21. Photograph of polished vertical section of banded manganese carbonate-oxide ore from 219 A7, natural size. a, green band; b, red band; c, barite.



219 B 5 limestone and those about to be described in beds 219 A 11 and 219 A 13, and are probably phosphatic pebbles in composition. The minerals in evidence in this bed are hematite, calcite, and barite. This bed is undoubtedly a manganiferous bed as shown by the oxi-



FIG. 22. Photograph of vertical polished section of banded manganese carbonate-oxide ore from 219 A7, natural size. a, red band; b, brown band.

dized weathering products. The bed as a whole resembles 219 A 11 which to all appearances is suggestive of mineralized reworked material.

219 A 6 is somewhat fine-grained and gritty red shale, measuring 0.4 to 0.5 of a foot in thickness.

219 A 7 is the main manganese-bearing bed, measuring .7 of a foot in thickness. This bed is of more than usual interest in that the manganese occurs as primary carbonates and oxides in the form of thin jasper-like bands of green and light chocolate brown color, and as lenticles, and nodules. Interlaminated with the jaspery bands are reddish bands with manganese essentially in the form of an oxide and a carbonate (Fig. 20, 21, and 22). This bed has been divided into three layers, a, b, and c. The lowermost or a subdivision is the reddish band which is essentially a manganiferous shale. It is nodu-

lar with nodules, lenticles, and bands of the green jaspery carbonate and oxide of manganese. Wherever the jaspery minerals occur in the red band, whether as nodules, lenticles, continuous or non-continuous bands, they present or suggest concretionary characteristics. The red bands are locally pyritiferous and barytic. Red shale occupies the greater portion of the bed.

Microscopic examination of this red band brings out very little, other than that it is distinctly hematitic with the hematite occurring as a pigment or as irregular accumulations (Fig. 23, Slide 276).

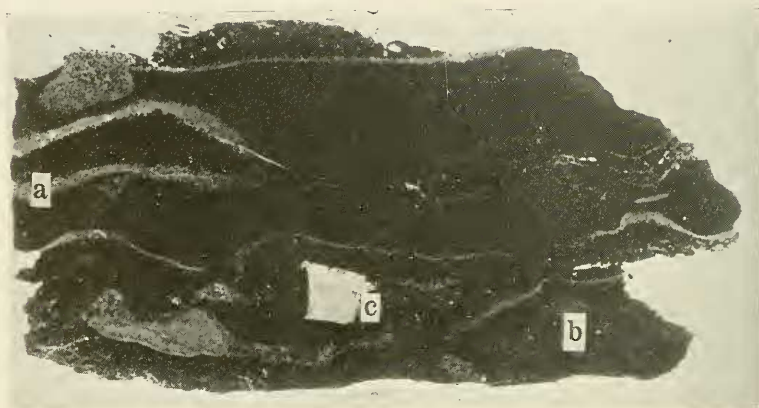


FIG. 23. Microphotograph of banded manganese ore with barite, from 219 A7; slide 276; enlarged 9.5 diam. a, red band; b, green band; c, barite.

The chemical analysis of this band is as follows:

ANALYSIS E.		ANALYSIS E I.	
<i>Red Bands.</i>		<i>Recalculation.</i>	
SiO <sub>2</sub> .....	27.61	MnO .....	19.71
Fe <sub>2</sub> O <sub>3</sub> .....	4.25	MnCO <sub>3</sub> .....	10.23
FeO .....	1.69	MgCO <sub>3</sub> .....	7.25
Al <sub>2</sub> O <sub>3</sub> .....	6.96	CaCO <sub>3</sub> .....	7.50
MnO .....	26.05	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .....	10.31
CaO .....	9.94	SiO <sub>2</sub> .....	19.44
MgO .....	3.49	H <sub>2</sub> O .....	1.87
P <sub>2</sub> O <sub>5</sub> .....	4.71	2H <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> + FeO ....	19.01
H <sub>2</sub> O .....	4.73	Fe <sub>2</sub> O <sub>3</sub> .....	4.25
CO <sub>2</sub> .....	10.57		99.57
	100.00		

Of most interest in connection with this red shaly band are the jaspery bands of green and brown carbonate and oxide of manganese. Where in bands, they vary from  $\frac{1}{8}$  inch to 1 inch  $\pm$  in thickness and may be continuous. The contact with the red band may be very even or very undulatory. This wavy character may be present whether the band thickens or thins or is of the same thickness throughout. The brown and green jaspery bands may contain thin laminae or nodules of other colors.

The green material is characterized by its chalcedonic and somewhat waxy luster, its translucency on thin edges, its hardness of 5 to 6, its specific gravity of about 3.13 (that of the green nodule) and its slight response to HCl.

The chemical analysis of this material is as follows:

ANALYSIS A.		ANALYSIS A I.	
<i>Green Band.</i>		<i>Recalculation.</i>	
SiO <sub>2</sub> .....	7.24	MnCO <sub>3</sub> .....	44.39
Fe <sub>2</sub> O <sub>3</sub> .....	3.36	MnO <sub>2</sub> .....	8.68
FeO .....	3.21	CaCO <sub>3</sub> .....	20.11
Al <sub>2</sub> O <sub>3</sub> .....	6.11	MgCO <sub>3</sub> .....	4.21
MnO .....	35.53	FeO .....	3.36
CaO .....	11.30	H <sub>2</sub> O .....	.86
MgO .....	2.30	2H <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> + FeO ....	18.24
H <sub>2</sub> O .....	2.98		99.25
CO <sub>2</sub> .....	28.06		
	100.09		

The green band so very similar chemically to the green nodule already described in connection with the nodular bed lower down in the series, is in great part a rhodochrosite in composition but has in combination, in descending order of abundance, considerable amounts of calcareous, argillaceous and ferruginous material. Manganese not combined with CO<sub>2</sub> probably exists as some oxide, probably a peroxide, as considerable chlorine was given off by the sample when first treated with concentrated HCl. Other features hardly need any explanation.

Thin sections of this band are very unsatisfactory in that, because of the impalpable fineness of the grain, little can be seen outside of structural features and certain opaque minerals, chiefly hematite.



The brown band differs in chemical composition, in color, and in specific gravity. The color is a light or dark chocolate brown. The specific gravity is 3.32. The chemical composition differs mainly in the higher percentage of manganese, as shown in the following analysis:

ANALYSIS D.		ANALYSIS D I.	
<i>Brown Band.</i>		<i>Recalculation.</i>	
SiO <sub>2</sub> .....	10.23	MnO .....	28.93
Fe <sub>2</sub> O <sub>3</sub> .....	1.32	MnCO <sub>3</sub> .....	32.89
FeO .....	.89	CaCO <sub>3</sub> .....	14.01
Al <sub>2</sub> O <sub>3</sub> .....	4.84	MgCO <sub>3</sub> .....	5.90
MnO .....	49.25	2H <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> .....	11.08
CaO .....	8.11	SiO <sub>2</sub> .....	5.40
MgO .....	3.02	Fe <sub>2</sub> O <sub>3</sub> .....	1.27
H <sub>2</sub> O .....	1.31		99.48
CO <sub>2</sub> .....	21.83		
	100.80		

Members **b** and **c** of bed **219 A 7** differ from the subdivision just described in the greater abundance of jaspery bands in comparison with the red shaly band and they show greater continuity on the whole.

Member **d** consists of green and brown jaspery bands all more or less nodular and interlaminated with the red manganiferous shale. Barite as segregations, disseminated blades, and veins occur infrequently. In the weathered portions of the section this bed is found altering on its more exposed structural planes to the secondary oxides of manganese such as psilomelane, etc.

**219 A 8** is a purplish manganiferous nodular shale measuring 0.3 of a foot in thickness. It contains lenticles and discoidal nodules of the green jaspery manganese carbonate (Fig. 24, Slide 284). The noticeable microscopic features of a thin section of this rock are its nodular, oölitic and shaly structures. The spherules, though rudely formed, are of either hematite or a carbonate, the former more closely associated with the green jaspery structures, and the latter with the red shale.

**219 A 9** is a manganiferous bed structurally, mineralogically, and, presumably, chemically, analogous to **219 A 7**, and measuring .5 of a

foot in thickness. Green discoidal nodules of manganese carbonate and the green, brown and red manganiferous bands similar to those of 219 A 4 are a conspicuous feature of the bed. A thin section from one of the nodules of this bed collected during the summer of 1912 shows, aside from the nodular form, conspicuous zonal and

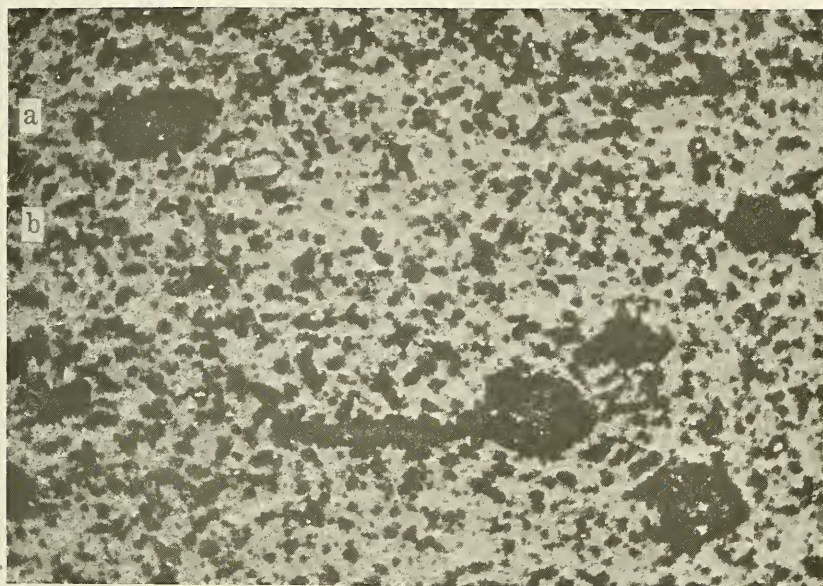


FIG. 24. Microphotograph of red shale from 219 A8; slide 284; enlarged 38 diam. a, hematite aggregation; b, spherules of hematite.

oölitic structures. For the most part the grain is impalpable, but that of the core is more or less crystalline. There are five pronounced parts consisting of a crystalline innermost core, No. 1, which in a great part is composed of carbonate, presumably that of calcium and manganese though nothing of a definite confirmatory nature could be observed, and 4 successive enveloping shells differentiated from each other by either the presence or absence of hematite, the shade or intensity of color or by fineness of grain. The oölitic character of zones 3 and 5 with spherules consisting in great part of hematite and measuring as small as 12 microns and as large as 90 is very noticeable. Layers 2 and 4 in a great degree consist of

indeterminate material (Fig. 25, Slide 244). Anisotropic minerals in this section are not common but those most noticeable are calcite.

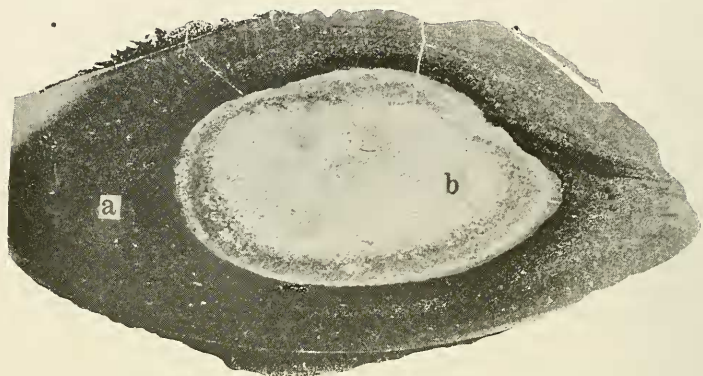


FIG. 25. Microphotograph of nodule, from 210 A7; slide 244; enlarged 4.0 diam. a, outer zone of manganese carbonate; b, core of crystalline manganese carbonate.

barite, and chlorite, the latter being usually associated with the barite.

219 A 10 consists of 3.5 feet of alternate layers of purple and green shale which contain thin nodules and lenticles of jaspery manganese carbonate, some of which measure 1.3 feet in length and 0.1 feet in thickness. The lowermost subdivision of this bed, 210 A 10a, is a dark reddish-green heavy nodular and oölitic shale with nodules very similar to those described above. Disseminated minute reddish mineral particles suggesting hematite spherules are found rimming the nodules in some cases. Barite occurs occasionally. Subdivision b of this bed is composed of 0.2 of a foot of green and red lenticular manganiiferous seams with green jaspery nodules, similar to those in the lower beds, interlaminated with a hematic oölitic shale. Subdivision c, measuring 0.5 of a foot in thickness, is a dark gray oölitic and slightly nodular shale with green jaspery seams. Barite blades occur with nodular accumulations of manganiiferous calcite. Microscopically this layer is essentially a hematitic oölitic shale with the individual spherules measuring from 15 to 23 microns in diameter while larger aggregations of spherules measure from 0.253 mm. to 0.387 mm. in diameter. The spherules consisting of hematite and car-



bonate are found in a groundmass the character and composition of which is for the most part indeterminable. Occasional pyrite grains are found (Fig. 26, Slide 280).

**219 A 10d**, the upper subdivision, consists of 0.3 of a foot of nodular and oölitic dark gray shale with thin jaspery manganese carbonate laminations.

Subdivision **e** is a dark green nodular and oölitic shale, 0.8 of a foot in thickness and not very different from the layer **d** just de-

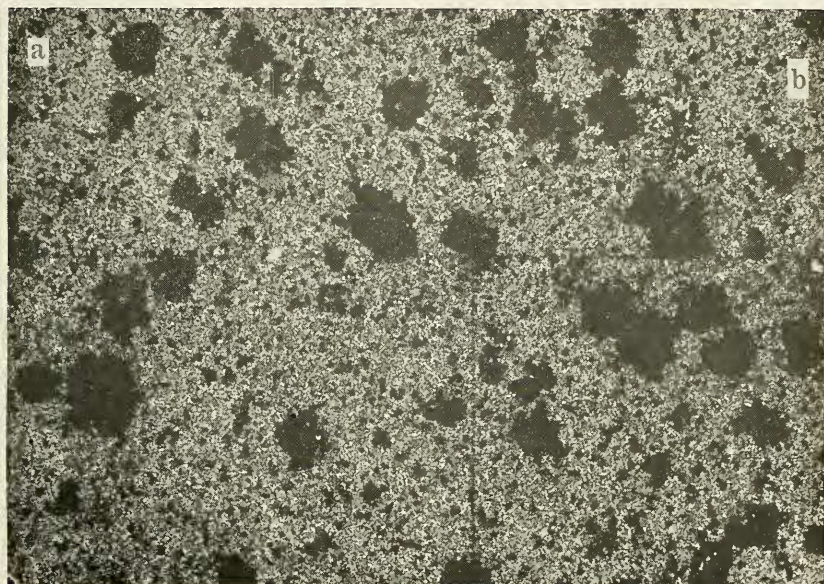


FIG. 26. Microphotograph of oölitic manganiferous shale from 219 A10c; slide 280; enlarged 22 diam. **a**, hematite spherules; **b**, shale with disseminated hematite.

scribed, and **f**—is a coarse nodular seam, 0.8 of a foot in thickness, in a dark green shale, comprising the uppermost portion of this bed.

**219 A 11** is a heavy tough reddish band, 0.5 of a foot in thickness and lithologically very different from the immediately overlying and underlying beds. For the most part, the structure is both somewhat nodular and oölitic. The general fragmentary nature of the fossils and of certain nodular or pebbly forms leads one to think

that this layer consists in some degree of reworked material. The surface of this bed shows ripple marks. The predominant constituents which a macroscopic examination affords are calcite, barite, argillaceous material, limonite, manganese oxide, and pyrite. Outside of the nodular, oölitic, and fragmentary character of the layer,

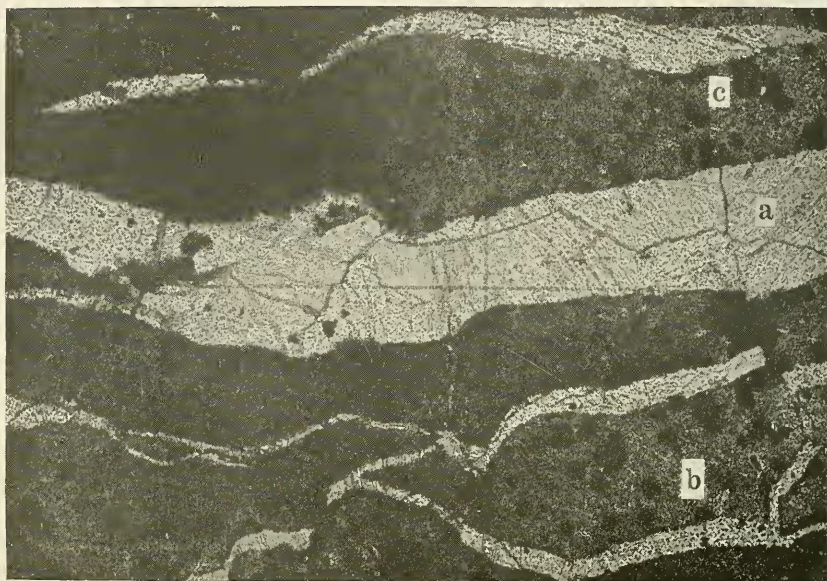


FIG. 27. Microphotograph of manganiferous red shale from 219 A11; slide 277; enlarged 22 diam. a, calcite vein; b, hematite spherule.

very little additional information concerning this peculiar rock could be gained microscopically (Fig. 27, Slide 277). The spherules are of two kinds, hematite and carbonate, and they average about 48 microns in diameter. Non-ferruginous portions of the slide show a groundmass of such fine-grained green material that very little could be made of it. *Hyolithes*, sponge spicules, and shell fragments partially or entirely replaced by calcite are a noticeable feature. Barite as scattered blades partially replaced by chlorite and pyrite, hematite as the chief constituent of the spherules, and carbonate are the most abundant of the determinable constituents of the slide (Fig. 28, Slide 278).

The chemical analysis of this rock is as follows:

ANALYSIS F.		ANALYSIS F 1.	
219 A 11.		Recalculation.	
SiO <sub>2</sub> .....	18.42	MnO .....	9.36
Fe <sub>2</sub> O <sub>3</sub> .....	6.33	MnCO <sub>3</sub> .....	19.22
Al <sub>2</sub> O <sub>3</sub> .....	7.95	CaCO <sub>3</sub> .....	18.61
MnO .....	21.44	MgCO <sub>3</sub> .....	10.54
CaO .....	14.46	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .....	7.50
MgO .....	5.01	Fe <sub>2</sub> O <sub>3</sub> .....	6.22
P <sub>2</sub> O <sub>5</sub> .....	3.46	SiO <sub>2</sub> .....	9.18
H <sub>2</sub> O .....	2.58	2H <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> .....	19.61
CO <sub>2</sub> .....	21.20		100.24
	100.85		

This bed is essentially a manganiferous argillaceous dolomite with considerable percentages of barite, hematite, and phosphate. It would seem quite reasonable to suppose that the phosphate Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> exists in the nodular portion as we have found to be the case in the nodules of 219 A 13 to be described later.

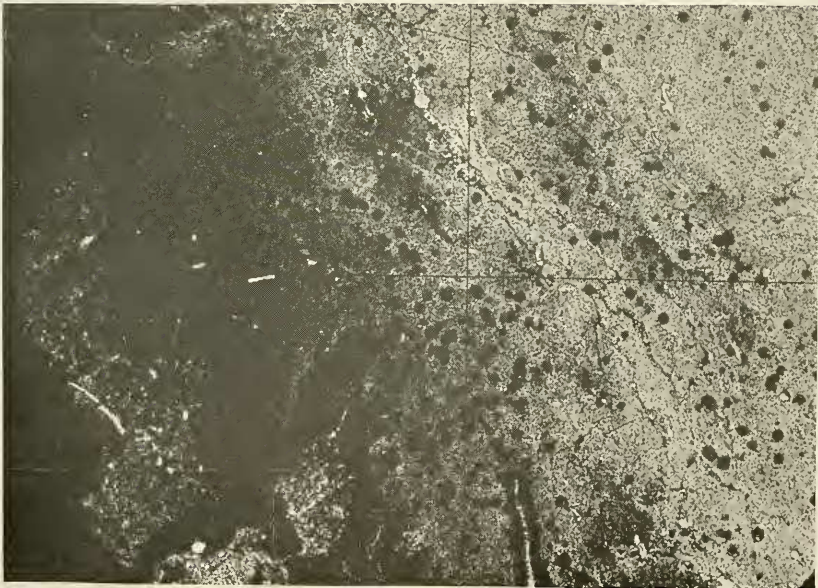


FIG. 28. Microphotograph of red manganiferous shale from 219 A 11; slide 278; enlarged 22 diam.; showing hematite spherules in a groundmass of manganese carbonate.



**219 A 12** is a fissile green shale measuring 1.4 feet in thickness with conspicuous black nodules which on weathering become white. Because of the similarity in form and color with those of **219 B 5**, **A 5**, **A 11**, and those to be described from the bed immediately above this one, the suggestion is made here that these nodules also may be phosphatic.

**219 A 13** is a phosphatic nodular manganiferous calcareous shale bed, 1 foot thick, with the nodules common in both bottom and top portions of the bed (Fig. 29). The nodules because of their white



FIG. 29. Photograph of a polished vertical section of a phosphatic nodular shale seam, **219 A13**; natural size. **a**, phosphatic nodule; **b**, shale with trilobite fragments.

weathering and subspherical to elongated form resemble those of **219 A 12**, **A 11**, **A 5**, and **B 5**. In chemical composition the nodules of this bed resemble those from the Cambrian of southern New Bruns-

wick described by W. D. Matthew (15). The chemical analyses of the Manuels brook and the New Brunswick phosphate nodules are as follows:

## ANALYSIS H.

*Manuels Brook, N. F.**Hanford Brook, N. B.*

SiO <sub>2</sub> .....	25.20	SiO <sub>2</sub> .....	24.74
Al <sub>2</sub> O <sub>3</sub> .....	7.67	Al <sub>2</sub> O <sub>3</sub> .....	11.85
Fe <sub>2</sub> O <sub>3</sub> .....	10.13	Fe <sub>2</sub> O <sub>3</sub> .....	11.44
CaO .....	23.50	CaO .....	22.35
MgO .....	4.78	KO .....	0.59
P <sub>2</sub> O <sub>5</sub> .....	17.68	MgO .....	2.29
H <sub>2</sub> O .....	2.71	NaO .....	1.41
CO <sub>2</sub> .....	2.23	P <sub>2</sub> O <sub>5</sub> .....	14.99
	93.90	H <sub>2</sub> O .....	3.43
			3.44
		CO <sub>2</sub> .....	3.53
			100.00

The similarity between the percentages of SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO and P<sub>2</sub>O<sub>5</sub> of the two analyses is at once very noticeable and at the same time very suggestive. It is hoped that at some future time, work of a correlative nature may be taken up in connection with these interesting and genetically problematical nodules. Among the macroscopically observable minerals in the fresh and altered rock are pyrite, hematite, limonite, wad or psilomelane, and vivianite in an argillaceous dolomitic groundmass. *Hyolithes* fragments are in abundance.

As no apparent manganese was observable in the considerable thickness of overlying green shales, 219 A 13 was considered to be the top of the manganese zone at Manuels Brook. According to Prof. van Ingen the *Paradoxides* fauna begins in these shales which immediately overlie the manganese zone.

TOPSAIL.—The manganese at Topsail some 4 miles east of Manuels (see Figs. 1 and 30) occurs interbedded in steep northerly dipping (50° to 78°) lower Cambrian strata consisting of shales, limestones and sandstones. The manganese is found in several beds of which only one measuring 1.4 feet in thickness seems to be of sufficient importance to have warranted prospecting, as shown by

some open cutting. This is a carbonate-oxide ore of manganese of brown color and vitreous luster.

Not only does the character and structure of the manganese at Topsail differ from that of Manuels but the section shows some



FIG. 30. Photograph of the open cut with the manganese prospect tunnel at Topsail; Loc. 219 E.

lithological variations. Moreover the rocks of the section are very much disturbed with the rapid changes in the dip of the beds. The structural changes in these beds are no doubt due to the great fault, the plane of which passes about 300 feet east from the manganese zone with a strike of N. 13 E. and a vertical dip. The fault plane lies between the Huronian and the lower Cambrian, and the beds immediately adjacent are considerably disturbed and so to a lesser extent are those farther away.

That a better idea may be obtained as to the relationship of the manganese, the following general and local stratigraphic sections with descriptions are given. The generalized section as worked out by Prof. van Ingen and Mr. A. O. Hayes during the summer of 1912 is as follows:



Loc. Number.

- 210 E 10 Brown shales with manganese at base ..... Open cut  
 9 Brown shales with limestone at base.  
 8 Heavy limestone.

	Ft.
7 Shaly limestone .....	6.0
6 Brown sandstone with limestone nodules .....	3.0
5 Fine and coarse sandstone with small limestone nodules..	6.0
4 Much sheared brown shale with limestone nodules and manganese at base .....	4.0
3 Mouth of tunnel and rotten zone .....	15.0
2 Coarse sandstone .....	6.0
1 Shear zone .....	0.3 to 0.5
0 Pre-Cambrian .....	25.0

It is quite apparent from a study of the above section that the lower Cambrian at Topsail is in many respects similar to that of Manuels. The absence of a basal conglomerate and the presence of sandstone are the most striking features of the associated beds. During the summer of 1913 a more detailed study of the manganese zone of 210 E 10 of the generalized section was made and the following subdivisions were made:

Loc. Number.

Ft.

- 219 E 7 Green shale, badly broken.  
 6 Banded, concentric and nodular shale ..... 1.0  
 5 Green shale, badly sheared ..... 0.5  
 4 Manganese oxide-carbonate ore ..... 1.4  
 3 Broken nodular green shale with manganese stain ..... 0.7  
 2 Calcareous manganiferous shale ..... 0.3  
 1 Hard nodular olive green shale, badly weathered and sheared,  
 with manganese stain.

Of this series two beds, 219 E 4 and 6, are worthy of more detailed description.

**219 E 4** is an oxide-carbonate ore of manganese of 1.4 ft. in thickness. It is irregularly banded and nodular, of chocolate-brown color, somewhat vitreous in appearance and argillaceous, with a hardness of 5 to 6 and specific gravity of 3.26. Disseminated

through the ore are irregular small areas of a pink carbonate resembling rhodochrosite in physical characteristics, and barite. The ore is incrustated with psilomelane as an oxidation product. Microscopic examination brings out a coarsely banded and nodular structure with a groundmass of indeterminate material which is for the most part homogeneous to all appearances and of brown color.



FIG. 31. Microphotograph of barite sheaf in manganese oxide-carbonate ore from 219 E4; slide 269; enlarged 22 diam. a, barite sheaf; b, manganese oxide-carbonate ore.

The color of this ore is due to the brown and black oxides of manganese and iron. Conspicuous among the anisotropic minerals are barite which occurs as blades or bundles of blades generally replaced by chlorite, and calcite, all very much discolored by the manganiferous and ferruginous oxides. Minute veins of discolored calcite are present (see Fig. 31, Slide 269).

The chemical analysis of the ore and its recalculation are as follows:

ANALYSIS I.		ANALYSIS I I.	
219 E 4		Recalculation.	
SiO <sub>2</sub> .....	18.04	MnO <sub>2</sub> .....	34.25
Fe <sub>2</sub> O <sub>3</sub> .....	4.82	MnCO <sub>3</sub> .....	11.27
Al <sub>2</sub> O <sub>3</sub> .....	6.58	CaCO <sub>3</sub> .....	4.00
MnO .....	41.26	MgCO <sub>3</sub> .....	4.97
CaO .....	2.24	SiO <sub>2</sub> .....	10.32
MgO .....	2.39	BaSO <sub>4</sub> .....	5.40
BaSO <sub>4</sub> .....	5.40	Fe <sub>2</sub> O <sub>3</sub> .....	4.82
CO <sub>2</sub> .....	8.34	2H <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> .....	16.30
H <sub>2</sub> O .....	7.98	H <sub>2</sub> O .....	5.41
	97.05		96.74

This is essentially a hydrous oxide of manganese with considerable amounts of argillaceous material, rhodochrosite, silicious matter, dolomite, barite and hematite in descending order of abundance.

**219 E 6**, not a manganese ore bed, though manganiferous, is of interest mineralogically and petrographically. In structure it is concretionary and banded, nodular and microscopically oölitic. It is essentially a calcareous, ferruginous and manganiferous nodular and banded shale (see Fig. 32). Under the microscope the greater part of the groundmass, isotropic under crossed nicols, is of indeterminable composition simulating phosphatic material. Of the anisotropic minerals, calcite is most frequent and occurs with other carbonate material in bands which show an oölitic structure. The individual spherules, subspherical to elliptical in form show either concentric or radiated structure, the latter showing an interference cross with crossed nicols (Fig. 33, Slide 272). Calcite frequently has the curved twinning planes indicative of strain. Barite occurs in narrow veins or bands, as disseminated blades, or as sheath-like blades or aggregations, usually being replaced to a greater or less extent by chlorite and in a few instances by pyrite (Fig. 34, Slide 272). The spherules consist of hematitic pigment, carbonate and chlorite. Because of the frequent association of chlorite with barite one is led to suspect that possibly the chlorite spherules were originally of barite which has since been replaced by the chlorite. Other spherules made up in great part of hematite, sometimes show-





FIG. 32. Photograph of polished vertical section of banded and nodular shale from 219 E6; natural size. a, green shale; b, hematite nodule in hematite band; c, ferromanganese concretion; d, phosphatic nodule.

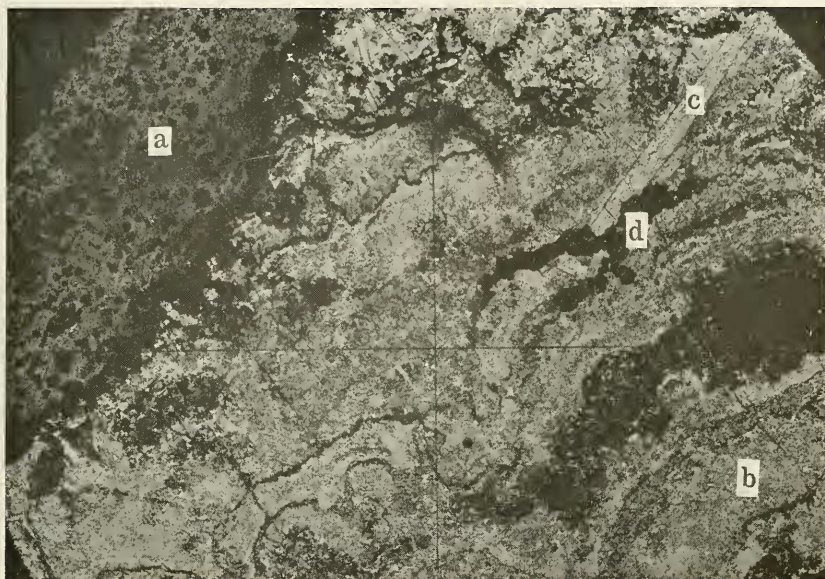


FIG. 33. Microphotograph of banded and nodular shale from 219 E6; slide 272; enlarged 38 diam. a, oölitic hematite shale; b, carbonate calcite band; c, barite; d, pyrite.



FIG. 34. Microphotograph of barite with chlorite replacement from 219 E6; slide 272; enlarged 22 diam. a, barite; b, chlorite replacing barite; c, phosphatic? material.

ing carbonate centers, are found most frequently in the jaspery bands. The spherules vary in size from 12 to 120 microns but have average diameter of about 94 microns.

The chemical analysis of this bed, with its recalculation, is as follows:

<i>219 E 6.</i>		<i>Recalculation.</i>	
SiO <sub>2</sub> .....	18.24	MnCO <sub>3</sub> .....	16.79
Fe <sub>2</sub> O <sub>3</sub> .....	10.01	CaCO <sub>3</sub> .....	20.91
Al <sub>2</sub> O <sub>3</sub> .....	14.52	MgCO <sub>3</sub> .....	10.57
MnO .....	10.42	FeCO <sub>3</sub> .....	4.52
CaO .....	13.74	Fe <sub>2</sub> O <sub>3</sub> .....	5.49
MgO .....	4.94	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .....	3.75
P <sub>2</sub> O <sub>5</sub> .....	1.71	SiO <sub>2</sub> .....	1.20
CO <sub>2</sub> .....	24.01	2H <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> .....	36.38
H <sub>2</sub> O .....	2.07		99.61
	<u>99.66</u>		

From the above analysis, this rock is essentially a dolomitic manganiferous ferruginous shale with considerable amounts of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. Among the microscopically observable minerals in the above recalculation are calcite, hematite, quartz. The nodular portions, usually isotropic and of exceedingly fine grain, are probably

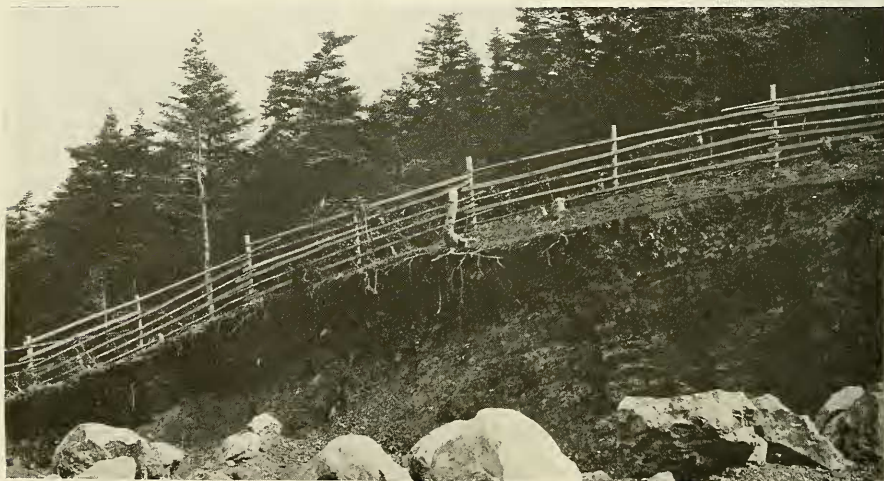


FIG. 35. Photograph of manganese prospect along the Kelligrews highway just south of Long Pond; Loc. 219 F.



# Long Pond

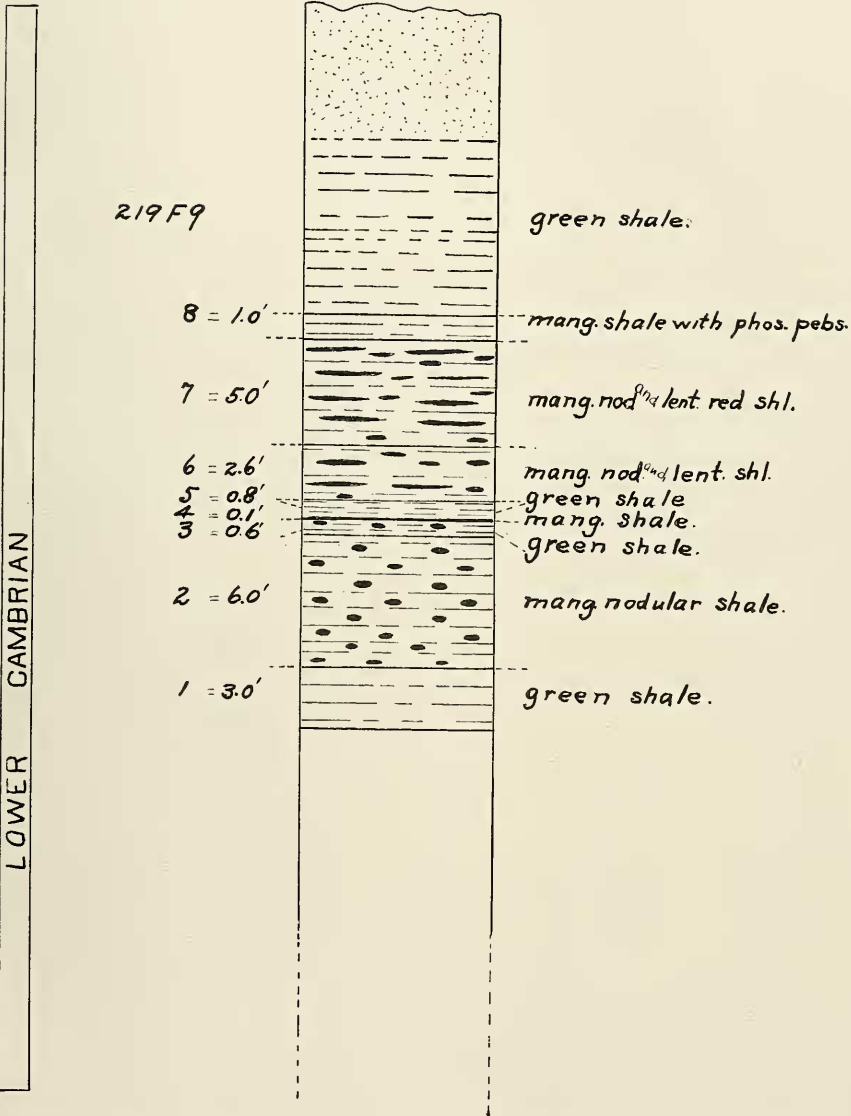


FIG. 36. Columnar section of the manganese zone at Long Pond; Loc. 219 F.

in great part shaly in composition. The nodules of this band suggest a very possible analogy to those of 219 A 5, 11, 12, 13, and B 5. In as much as this bed is somewhat phosphatic, the phosphate in all likelihood is associated with the nodules, as is the case with the nodules of 219 A 13 of Manuels. This bed is structurally and mineralogically quite similar to the phosphatic beds of Manuels.

**LONG POND SECTION.**—About  $2\frac{1}{2}$  miles southwest of Manuels and west of the railroad and wagon road (see Fig. 35), manganese occurs, in a low cliff, as nodular and banded layers interbedded with shales. Though the manganiferous beds at this locality are considerably more oxidized than those at Manuels, the occurrence as a whole is similar and it is necessary to present the section with only brief macroscopical descriptions of the important beds (Fig. 36).

Loc. Number.

Ft

219 F 10 Glacial mantle.

9 Manganiferous green shale.	
8 Phosphatic nodular manganese shale .....	1.0
7 Manganiferous nodular and lenticular green shale .....	5.0
6 Banded nodular ore .....	2.6
5 Fissile green shale .....	0.8
4 Manganiferous banded ore .....	0.1
3 Massive nodular green shale .....	0.6
2 Nodular shale .....	6.0
1 Heavy green olive shale .....	3.0

**219 F 2** of the above section corresponds quite closely to the lower nodular bed, 219 A 4a, of Manuels (see page 392), chiefly because of the presence of abundant discoidal-shaped nodules identical with those at Manuels. The nodules have altered for the most part to a wad and clay, some having secondary manganese or white clay centers and clay border zones and others with limonitic green clay centers with secondary manganiferous clay border zones. The weathered nodules are very abundant.

**219 F 6** is a heavy manganiferous bed composed of several  $\frac{1}{2}$ " to 3" red, brown and green manganiferous seams separated by thin nodular shale laminations that are now red. It is quite evident that this bed is a continuation of either 219 A 7 or 10 of Manuels. The interior of some of the weathered nodules is a red and green residual clay. The manganiferous seams weather reddish and greenish.

219 F 7 is probably a continuation of 219 A 8 and 9 of Manuels inasmuch as this bed is nodular and has many lenticular and continuous jaspery seams of 0.1 inch to 1 inch in thickness alternating with  $\frac{1}{2}$  inch to 1 inch seams of reddish manganiferous shale.

219 F 8 from its similarity to 219 A 13 of Manuels may be described as a phosphatic nodular manganiferous shale with the manganese in evidence as some hydrous oxide.

CHAPEL COVE SECTION.—The manganese at Chapel Cove, of inconsiderable amount, occurs in a very much faulted series of lower Cambrian limestones and shales as alteration products on many of the structural planes. If it were not for certain lithological analogies with the deposits just described it would hardly seem necessary to give any detailed description of this deposit because of the small quantity of manganese present (see Figs. 1 and 37).

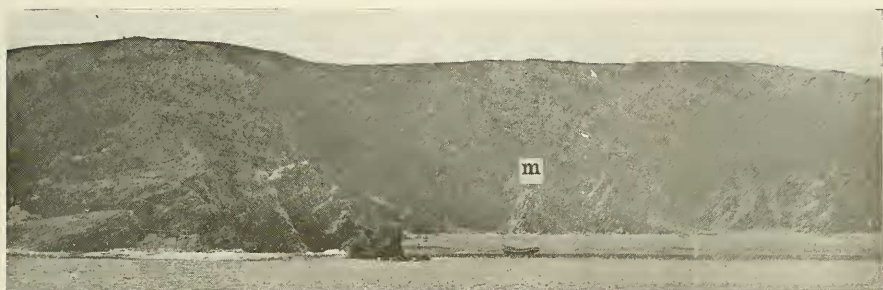


FIG. 37. Photograph of the section along the shore at Chapel Cove near Holyrood, Loc. 213 C; showing the managenese zone at (m).

The generalized section as worked out by Prof. G. van Ingen and Mr. A. O. Hayes during the summer of 1912 is as follows:

Loc. Number.	Ft.
213 C 4 c Olive green shale.	
b Alternate pink layers with small black pebbles, manganese layer	3.6
a Olive green shale, sheared near fault.	
C 3 Nodular limestone and shale .....	24.0
7 Argillaceous red limestone and alternating shales .....	25.0
6 Red shaly limestone .....	18.0
5 Red shale .....	8.0
D 7 Heavy red limestone .....	10.0
6 Red shales with limestone.	
5 Red and green limestone.	
4 Green limestone.	



- E 2 Gray limestone.
  - 1 Conglomerate with pebbles of syenite, black chert and limestone.
  - 0 Syenite.
- C 2 Agglomerate.
  - 1 Ribbon slates. Conception slates (Huronian).

The section represents the stratigraphic sequence and the locality numbers indicate the position of the layers. Quoting Prof. van Ingen in regard to this most interesting locality:

"It appears to me that we have here the remnant of a squeezed syncline, the northern margin of which has been shoved far northwardly onto the underlying agglomerate and ribbon slates."

213 C 4b was studied more in detail by the writer during the summer of 1913 in the hope that some more definite knowledge might be gained on the occurrence of the manganese at this point, but without very much satisfaction. The subdivided manganese bed is as follows:

Loc. Number.

- 213 L 4 c Finely banded nodular bed.
  - b Fractured and slickensided green shale.
- 213 L 4 a Black nodular calcareous green shale with manganese staining.
  - L 3 Nodular ferruginous calcareous green shale with manganese stains.
    - 2 Fractured and fissile shale.
    - 1 Manganiferous calcareous green shale with hematite and pyrite.

In as much as the manganese was not visible to any great extent in its primary form throughout this small series of 3 to 4 feet no analysis was thought necessary. Two of the above beds, 213 L 3 and 213 L 4 are worthy of macroscopical and microscopical descriptions because of marked lithological resemblance to certain of the rocks at Manuels.

213 L 3 is a nodular shale with conspicuous calcareous ferruginous and manganiferous aggregations and jet black pebbles or nodular forms. All structural and divisional planes of this bed are conspicuously stained with some secondary oxide of manganese, probably a hydrated oxide such as psilomelane. Microscopical examination of this shale brings out the fact that the structure is nodular and oölitic and that the rock is a ferruginous chloritic shale.

The groundmass consists of chlorite and, for the most part, of an indeterminable material. Calcite occurs as an alteration product or as a constituent of the hematitic spherules. Quartz is found composing infrequent aggregates and as vein-filling material. The opaque minerals other than hematite are manganese as psilomelane or some other secondary derivative, pyrite as disseminations, and



FIG. 38. Photograph of manganese prospect on Brigus South Head; Loc. 212 A12a. a, oxidized manganese beds; b, green shale.

limonite as a yellow staining. The spherules are for the most part hematite in composition but carbonate is a very common constituent. The diameters of the spherules range from 21 to 159 microns but average around 44 and 77 microns. The ferruginous centers of some of the spherules measure 0.8 of a micron.

Certain discoidal nodules in 213 L 4c resemble those of 219 A 4 at Manuels though they are very much less abundant.

213 L 4a is nodular and the texture exceedingly fine-grained and locally crystalline. The greater portion of the thin section is probably composed of shale material and the remainder is taken up in great part by calcite and carbonate disseminations, as replacement material of hyolithes shells, or as mineral aggregates. Barite occurs

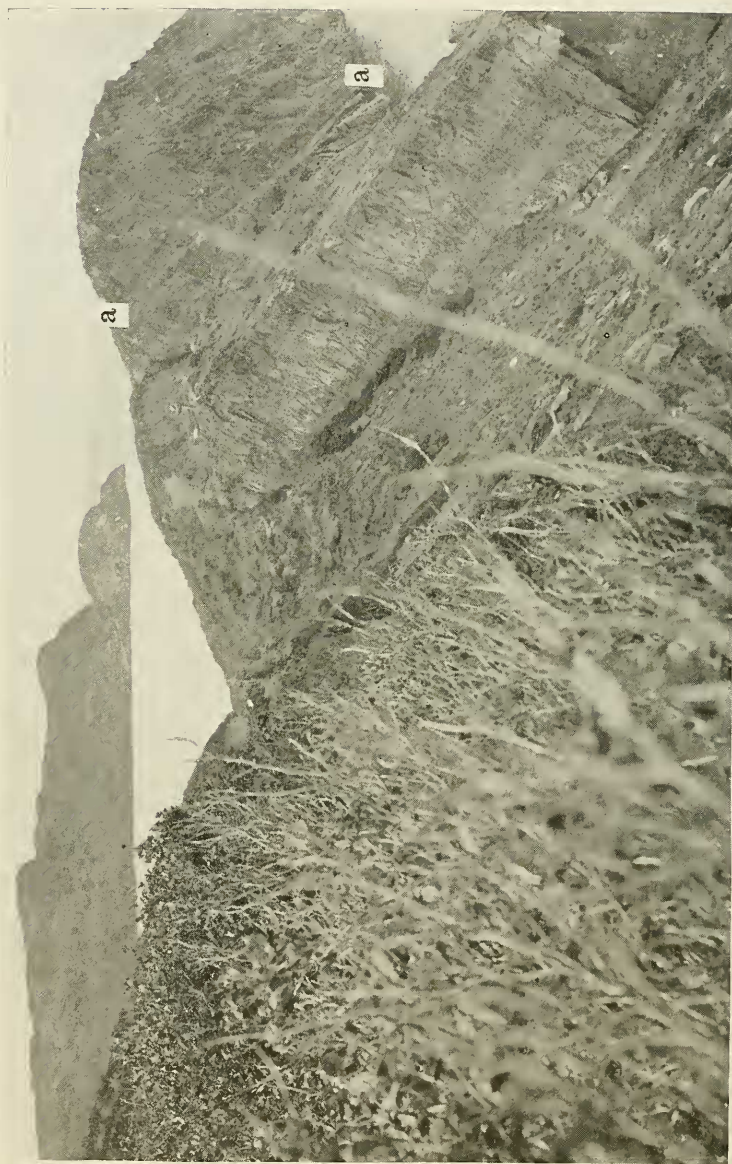


FIG. 39. View of Brigus South Head looking across the mouth of the harbor in a northerly direction and showing the position of the manganese zone (a-a).



as infrequent disseminations and individual platy crystals and probably once formed the *Hyolithes*-like rods now replaced by chlorite and a carbonate. Pyrite and hematite are found. The nodules of this bed, subspherical in shape, show under the microscope a compact



FIG. 40. View of the manganese beds (a) dipping into the sea on the east side of Brigus South Head.

structure and an almost impalpable fineness of grain. Under crossed nicols an occasional angular fragment of quartz is found but the groundmass as a whole appears to be isotropic. It is possible that these pebbles are analogous to the phosphate pebbles of Manuels, Topsail, and Long Pond.

BRIGUS SECTION.—At Brigus South Head on the west shore of Conception Bay (see Figs. 1, 38, 39, 40, and 41) manganese is found to a great extent in the oxidized state in several beds at the water's edge in the shales of lower Cambrian age which make up the sharp hog back ridge overlooking the "Needles." Because of the inac-

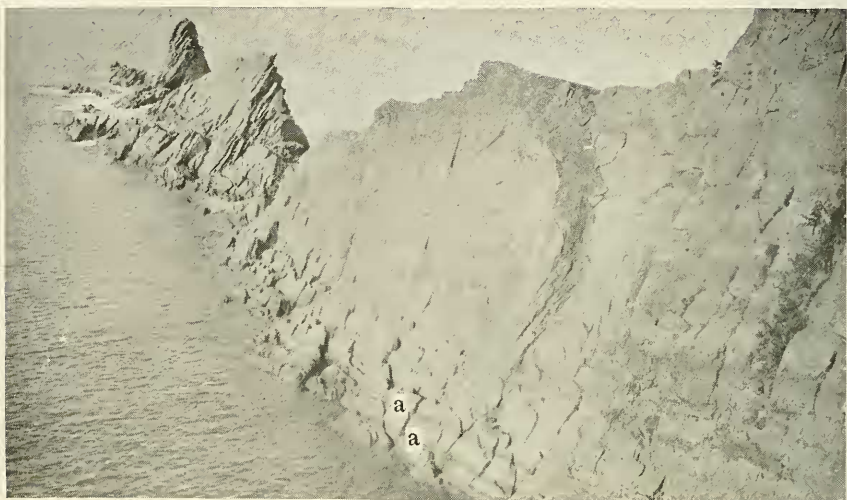


FIG. 41. View of the "Needles" at the extremity of Brigus South Head, showing the manganese zone (a-a).

cessibility of that portion of the ridge where the manganese was best preserved, detailed measurement of the section was not possible. Prof. van Ingen and Mr. A. O. Hayes in 1912 found that the best manganese measured about 4.5 feet thick in a zone of 15 feet. Specimens collected from more accessible portions were all practically altered to psilomelane but there is one which shows the original jaspery carbonate quite similar to the types described in connection with the Manuels occurrence. Several old prospect pits on the more accessible parts of this ridge were examined by the writer, but the manganese was found to be in its secondary state and the interbedded shales in a very much disturbed condition. The strike of the strata of this locality is N. 10 E. and the dip 47 E.

## Brigus

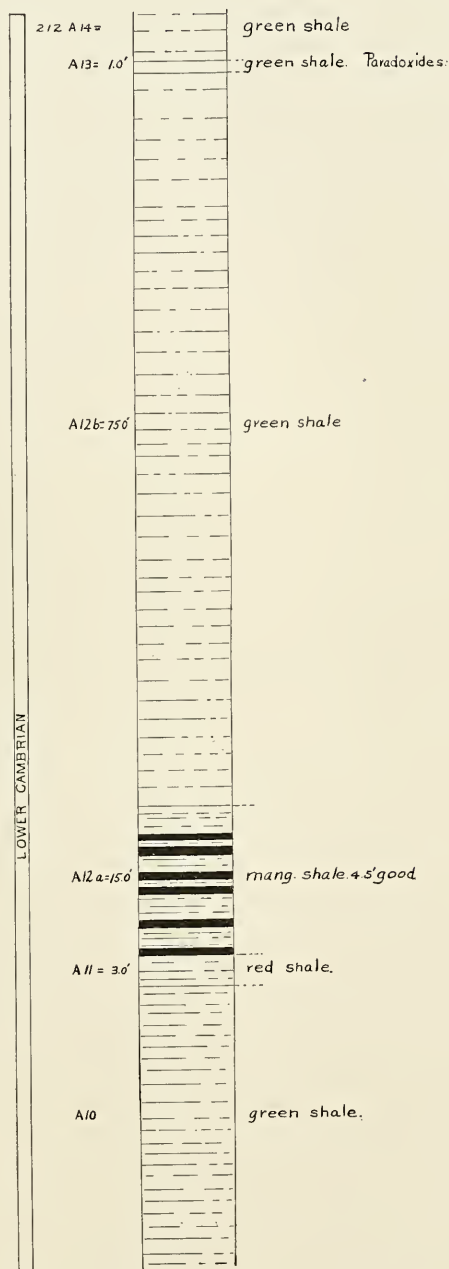


FIG. 42. Columnar section of a portion of the lower Cambrian at Brigus South Head, from measurements made by Gilbert van Ingen and A. O. Hayes, 1912.



The following section as prepared by Prof. van Ingen and Mr. A. O. Hayes from their study of the region in 1912 shows the stratigraphic relations of the manganese deposits at this point (Figs. 39 and 42).

Loc. Number.	Ft.
212 A 14 Green shales, end of needles .....	50.0
13 <i>Paradoxides</i> zone, green shales .....	1.0
212 A 12 b Green shales .....	75.0
12 a Manganese zone (4.5 ft. best) .....	15.0
11 Red shales, thin band .....	3.0
10 Green shale .....	60.0
9 Red shale .....	210.0
8 Red shaly limestone .....	11.6
7 Red shale .....	28.0
6 Limestone, heavy white at base, nodular and red above. <i>Holmia bröggeri</i> and other trilobites .....	30.0
5 Red shale .....	5.0
4 Limestone, very shaly .....	12.0
3 Red shale .....	32.0
2 Limestone with <i>Cryptozoon</i> .....	30.0
1 Red shale with local sandstone and conglomerate .....	50.0
Unconformity.	
0 Pre-Cambrian shale and ash beds.	

The striking feature of this section is the position of the manganese zone in relation to the *Paradoxides* bed which is exactly the relation established at Manuels and undoubtedly at the other localities described.

SMITH SOUND SECTION, TRINITY BAY.—The manganese zone on Trinity bay occurs at Smith Point (Fig. 1) as two massive beds associated with red and green nodular shales and limestones of lower Cambrian age. The accompanying map (Fig. 43), prepared from a transit survey of the shore line by Prof. van Ingen during the summer of 1913, shows the structural and stratigraphic relations of the two manganese beds, 230 D 20 and D 27. The general strike of these beds is north and the dip, 20 west.

230 D 27, the important manganese bed of this section (Figs. 44, 45), measures some 38 inches in thickness, and is faulted with a downthrow of 15 feet on the west side. It is the thicker of the two manganese beds, and has been found by analysis to be essentially a

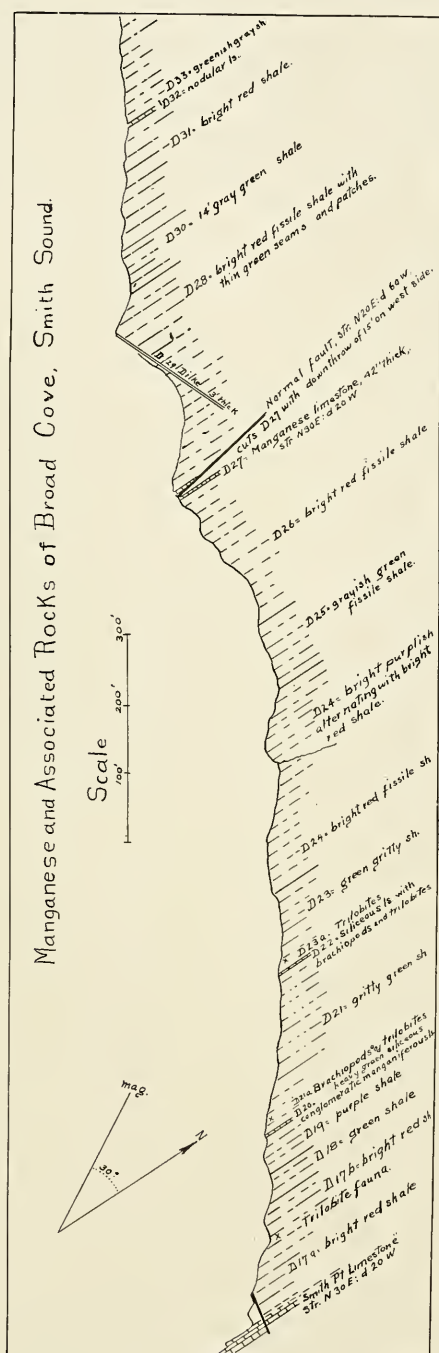


FIG. 43. Map of the outcrops of the protolenus and manganese zones exposed on the shore of Broad Cove, near Smith Point, Smith Sound, traced from field map based on stadia transit surveys by Gilbert van Ingen, 1913.

## Smith Point

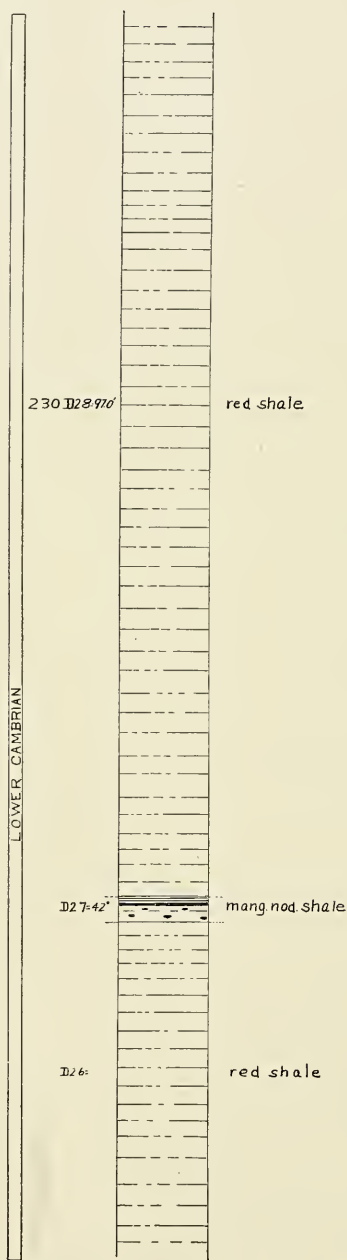


FIG. 44. Columnar section of a portion of the lower Cambrian at Broad Cove, near Smith Point, Smith Sound, Trinity Bay, Newfoundland, showing the manganese zone, 230 D26 to 28.



manganiferous dolomitic ferruginous shale. The bed is somewhat massive and nodular though the nodules are very irregular as compared with those at Manuels and other localities; irregular crystalline areas form the nodular portions while the matrix is made up of more argillaceous matter. Thin sections taken from the bottom and central portions of the bed were examined microscopically.

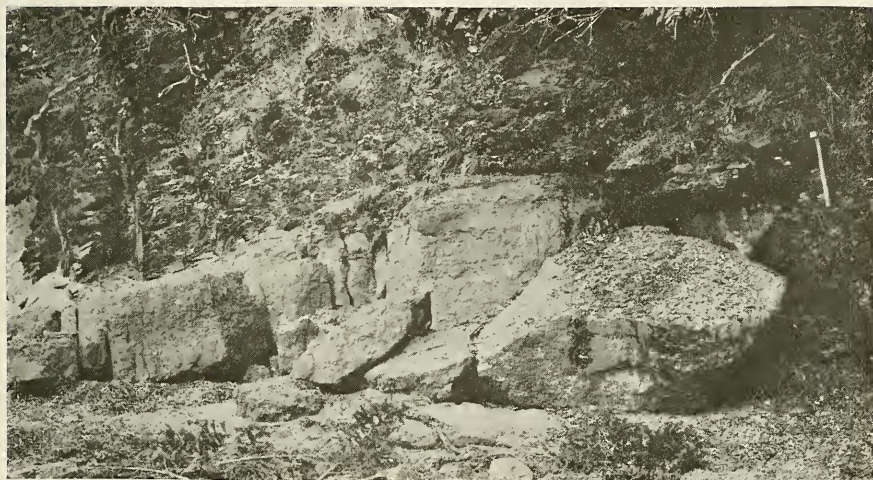


FIG. 45. Exposure of manganese ore, 230 D27, on the Broad Cove shore, near Smith Point, Smith Sound. This is a nodular ferro-manganese carbonate-oxide bed.

**230 D 27aa** is a reddish nodular and oölitic shale, with hematitic carbonate making up the greater portion of the determinable minerals; aggregations of a fine-grained dark material suggest phosphatic nodules so common in the Manuels occurrence. Irregular grains of quartz and aggregations of chlorite are found. Sections of trilobites and other organic forms containing carbonate material abound. Some hydrous manganic dioxide occurs (Fig. 47, Slide 299). Sections from the middle portions of the bed, **230 D 27e**, show a somewhat massive, nodular or oölitic reddish rock. Hematite is found as a pigment and to a lesser extent as lustrous opaque grains to which the color of the rock is due. A manganic oxide occurs as irregular and infrequent grains. Carbonate occurs as vein filling, as irregular areas, or as replacements of sponge spicules



FIG. 46. Nearer view of the ferro-manganese ore bed, 230 D27 on the Broad Cove shore.

and other organic bodies. Barite is found infrequently, sometimes with chlorite fringing it. Chlorite may be found replacing trilobite fragments.

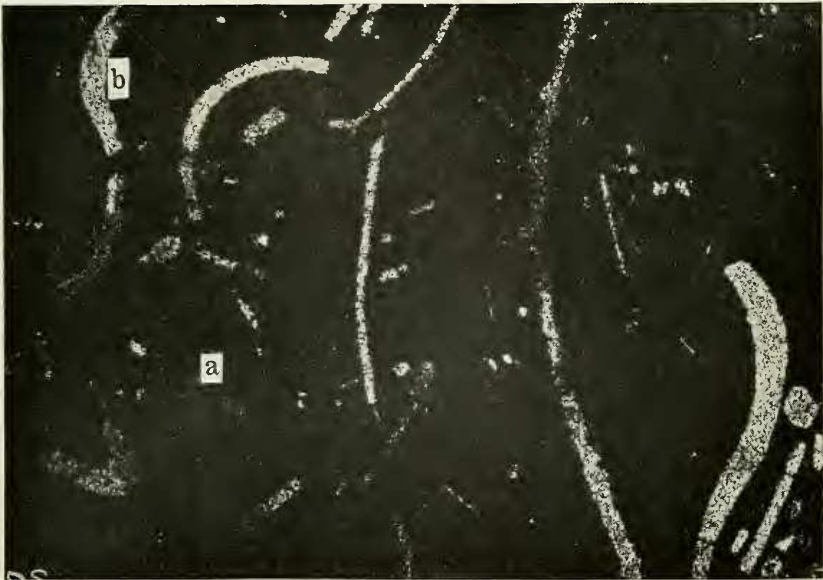


FIG. 47. Microphotograph of fossiliferous manganese ore, 230 D27; slide 299; from Broad Cove; enlarged 22 diam. a, manganese carbonate-oxide ore; b, fragment of trilobite test.

The following analysis and recalculation represent the chemical composition of an average sample of the bed and will corroborate some of the petrographic observations:

ANALYSIS K.		ANALYSIS K I.	
230 D 27.		Recalculation.	
SiO <sub>2</sub>	15.14	MnCO <sub>3</sub>	26.91
Fe <sub>2</sub> O <sub>3</sub>	9.22	MnO <sub>2</sub>	9.00
Al <sub>2</sub> O <sub>3</sub>	12.04	CaCO <sub>3</sub>	15.21
MnO	25.63	MgCO <sub>3</sub>	7.75
CaO	10.04	Fe <sub>2</sub> O <sub>3</sub>	9.22
MgO	3.72	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	2.50
P <sub>2</sub> O <sub>5</sub>	1.26	SiO <sub>2</sub>	.84
H <sub>2</sub> O	2.73	2H <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>	30.06
CO <sub>2</sub>	21.05		101.49
	100.83		



The manganese according to the recalculation of the analysis is essentially in the form of a rhodochrosite and whatever manganese there is in excess probably exists as a peroxide. It is quite possible that  $\text{Ca}_3(\text{PO}_4)_2$  exists in the irregular black fine-grained areas, though nothing definite can be said in confirmation of it at this time.

SECTION OF THE LOWER CAMBRIAN FROM THE BASE OF THE LOWER  
PARADOXIDES ZONE DOWN TO THE TOP OF THE SMITH  
POINT LIMESTONE, TRINITY BAY (Fig. 47).

Loc. Number.		Ft.
230 D 32	Thin seams of nodular limestone in red shale .....	4.0
31	Bright red shale .....	46.0
30	Gray green shale .....	14.0
29	Dike .....	3.0
28	Bright red fissile shale with thin green seams and patches ....	97.0
27	Manganese limestone (manganiferous dolomitic shale) .....	3.5
26	Bright red fissile shale .....	78.0
25	Grayish green fissile shale .....	28.0
24	Bright purplish shale alternating with bright red shale .....	97.0
23	Green gritty shale .....	33.0
22	Gray band of fine grain silicious limestone full of pyrites and same brachiopods and trilobites .....	0.5
21	Gritty green shale, brachiopods and trilobites .....	62.0
20	Heavy green silicious conglomeratic manganiferous limestone	2.5
19	Purple shale .....	10.0
18	Green shale .....	10.0
17	Red shale .....	47.0
	b—Contains trilobite fauna .....	13.0 ft.
	a—Red shale .....	19.0
	Interval covered .....	15.0
16	Smith Point Limestone.	
	Total .....	535.5

V. OTHER MANGANESE DEPOSITS OF SOMEWHAT SIMILAR  
CHARACTER.

Sedimentary deposits of manganese are not of uncommon occurrence but it is rare that we find such deposits still in their unaltered condition as they were originally formed. There are however a few deposits elsewhere which in many respects resemble the Conception Bay and Smith Sound occurrences.

NEWFOUNDLAND, PLACENTIA BAY. In Placentia Bay, New-

foundland, manganese has been described by Murray and Howley as a massive carbonate bed interbedded with slates of "Silurian" age. Dr. T. Sterry Hunt (12: 204 and 205) described this mineral as

"compact and impalpable in texture, brittle, with a conchoidal fracture and a feeble waxy luster; slightly translucent on the thin edges; color fawn to pale chestnut-brown; streak white, hardness 4.0; density 3.25. The specimen shows faint lines which seem to be those of deposition and give to the mass the aspect of a sinter. It is encrusted and penetrated in parts with black crystalline oxide of manganese. The presence of oxide of manganese in this mineral is probably due to its partial decomposition." Analysis of this mineral by Dr. Hunt is as follows:

MnCO <sub>3</sub> .....	84.6
SiO <sub>2</sub> .....	14.40
Fe, CaO and MgO .....	traces

"This deposit is of interest on account of the existence of the metal in the form of a bedded carbonate. It probably represents the former condition of many of the oxide ores of manganese elsewhere in the stratified rocks, but they have since been converted to their more stable form."

It is quite evident from the above description of the Placentia Bay manganese that we have in all probability a deposit similar in mineralogic character and stratigraphic position to those in Conception Bay. No published stratigraphical or palæontological work has appeared on the Placentia Bay occurrences. In that portion of this paper relating to the stratigraphy of the manganese deposits it will be readily seen that the basin into which the manganiferous muds were deposited to form the present manganese beds of the lower Cambrian probably extended to or covered Placentia Bay or that portion of Placentia Bay where we now find Cambrian rocks. There is no doubt that the "Silurian rocks" referred to above by Howley and Murray are the lower Cambrian.

WALES.—Sedimentary manganese deposits have been described as occurring in the Cambrian rocks of Merionethshire, North Wales by Mr. Edward Halse (9: 156) in an article entitled, "The Occurrence of Manganese Ore in the Cambrian Rocks of Merionethshire." He says:

"in the Harlech mine, the bed of ore is a little over a foot thick, consisting of grit of medium grain, overlaid by a thin band of quartzite, probably meta-

morphosed grit. The roof proper consist of about 2 feet of very hard, schistose rocks, termed 'blue stone' by the miners. Specimens of ore taken from the mine are seen to be formed of uniform layers, having gray yellowish, white, greenish and chocolate-brown layers."

A reference by J. A. Phillips and Henry Louis (21:296) to the same occurrence is as follows:

"Beds of carbonate of manganese with some silicate, the outcrops of which have been to some extent changed into black oxide, occur intercalated between sandstones, grits and conglomerates of the Cambrian formation, and have been mined to some extent; the beds vary from one to two feet in thickness, and yield ore, averaging about twenty-seven per cent. of metal, which is used in spiegel making. These deposits are evidently symphytic and belong to group b of that class."

Phillips and Louis believe that these deposits were formed syngenetically but from precipitates in aqueous solutions. This deposit suggests very striking similarities to the Manuels occurrence not only mineralogically and genetically but also from the standpoint of stratigraphy.

ARKANSAS.—The Cason tract of the Batesville region, Arkansas, presents certain petrological analogies to the Newfoundland occurrences. Dr. Penrose (20:219) describes the ore as occurring

"in lenticular layers, varying from an eighth of an inch to three inches in thickness, and interstratified with an indurated red clay of a slaty structure. Generally, however, the ore occurs in the shape of flat, lenticular concretions, from a quarter of an inch to one inch in diameter, locally known as 'button ore.' They have a concentric structure, are dull black on the outside and bright on the inside and are imbedded in a red or brown, fine-grained and more or less calcareous sandstone."

Analyses of the ore run as follows:

Mn .....	34.64.....	50.41
Fe .....	4.88.....	7.56
SiO <sub>2</sub> .....	25.65.....	12.67
P <sub>2</sub> O <sub>5</sub> .....	0.58.....	0.06
Al <sub>2</sub> O <sub>3</sub> .....	3.79.....	1.37
CaO .....	5.13.....	2.09

Similar conditions to those postulated by Penrose for the accumulation of the manganese in the Arkansas region seem to me to be applicable to the Newfoundland deposits.



In writing of the circulation of the manganiferous solutions and the conditions under which they might be precipitated in the coastal shoals or lagoons, Penrose says (20: 590, 591):

"This gradual local accumulation of land and marine sediments would eventually cause shoals and possibly coastal lagoons and swamps, into which the waters from Archæan rocks of the Missouri Archipelago would drain."

"Here the solutions exposed in a stationary condition to the oxidizing and evaporating action of the atmosphere, would deposit their metalliferous contents as carbonate or possibly oxide of manganese. In some places considerable bodies of ore might be formed in one spot, in others the manganese would be dessiminated through the mechanical sediments being laid down at the same time. A secondary chemical action might cause the segregation of the disseminated manganese and the formation of concretions of carbonate of manganese, which would be later oxidized in forms such as are characteristically shown at the Cason mine, near Batesville, and elsewhere in the region. In other places the manganese might remain in a finely disseminated state, causing the common occurrence now seen throughout the region of an earthy manganiferous limestone containing from 3 to 15 per cent. of manganese."

SAXONY.—The writer was led to analyze certain of the manganese minerals from Schebenholz near Elbingerode in the Harz, which were purchased from Krantz, because of certain physical resemblances to the Newfoundland specimens. One specimen labelled "Allagite with Dialogite, etc." consists of three different materials; the first is greenish and gave the following analysis:

SiO <sub>2</sub> .....	39.10	MnSiO <sub>3</sub> .....	33.98
Fe <sub>2</sub> O <sub>3</sub> .....	1.87	MnCO <sub>3</sub> .....	15.05
Al <sub>2</sub> O <sub>3</sub> .....	10.79	MgCO <sub>3</sub> .....	12.64
MnO .....	27.69	CaCO <sub>3</sub> .....	1.70
CaO .....	1.00	SiO <sub>2</sub> .....	10.97
MgO .....	6.08	Fe <sub>2</sub> O <sub>3</sub> .....	1.75
H <sub>2</sub> O .....	1.13	2H <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> .....	23.76
CO <sub>2</sub> .....	13.13		99.85
	100.79		

Unfortunately the early descriptions of this substance were not quoted very fully by later writers, but one of the imported specimens which was similar to the one analyzed had the following original label pasted on the back of it:

Grüner Allagite in Tomosite  
eingewachsen.

73.71 Manganoxydulat.

16.00 Kieselerite.

7.50 Kohlensäure.

97.21

Schebenholz bei Elbingerode.

This analysis was published in 1817 and 1819 (Jashe 13: 1-12) and to all appearances is the same mineral analyzed by the writer, which is also labelled allagite.

Another part of the same specimen is a greenish jaspery mineral similar physically to the green band of the Newfoundland specimen and has the following composition:

*Recalculation.*

SiO <sub>2</sub> .....	76.40	SiO <sub>2</sub> .....	69.84
Fe <sub>2</sub> O <sub>3</sub> .....	.007	MnCO <sub>3</sub> .....	10.00
Al <sub>2</sub> O <sub>3</sub> .....	2.46	MnSiO <sub>3</sub> .....	8.00
MnO .....	10.53	MgCO <sub>3</sub> .....	3.79
CaO .....	1.62	CaCO <sub>3</sub> .....	2.80
MgO .....	1.81	2H <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> .....	6.11
H <sub>2</sub> O .....	.80		<u>100.54</u>
CO <sub>2</sub> .....	7.32		
	<u>100.947</u>		

According to the recalculation this material is a mangiferous argillaceous chert, and is in all probability the silicious schist or shale of the Culm referred to later on.

The third portion of the specimen analyzed is a pinkish sparry mineral occurring as small veins with the following composition:

*Recalculation.*

SiO <sub>2</sub> .....	7.10	MnCO <sub>3</sub> .....	76.13
Fe <sub>2</sub> O <sub>3</sub> .....	.62	MnSiO <sub>3</sub> .....	8.92
Al <sub>2</sub> O <sub>3</sub> .....	.76	CaCO <sub>3</sub> .....	4.00
MnO .....	52.01	MgCO <sub>3</sub> .....	2.44
CaO .....	2.26	SiO <sub>2</sub> .....	2.16
MgO .....	1.17	Fe <sub>2</sub> O <sub>3</sub> .....	.37
H <sub>2</sub> O .....	1.70	2H <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub> .....	5.98
CO <sub>2</sub> .....	32.20		<u>100.00</u>
	<u>97.82</u>		

This mineral, because of its similarity to another specimen with

a label which reads "Spathiger Diallogit" pasted on it, is probably diallogit. It is however a very impure rhodochrosite.

According to W. Holzberger (11: 383) and C. Zerrenner (25: ?—) the ores from the Kaiser Franz mine near Elbingerode, in the Harz, occur as pocket-shaped intercalations a meter or so thick in the silicious shales of the Culm. The ore consists of psilomelane in dense and botryoidal masses, some pyrolusite and coatings of wad, with rhodonite, rhodochrosite and quartz present as accessories. The ore formerly worked contained on an average 60 to 63 per cent. of manganese peroxide, sometimes rising to 67 per cent. (23: 250). Zerrenner considers these manganese ores as later material separated out of the silicious shales, a theory which needs further investigation. Though the above described deposit is not the same as that from which the specimens analyzed above came from, it is no doubt similar.

The Elbingerode occurrence is similar to the deposits of SE. Newfoundland in that they are both primary manganiferous sediments. They differ in that the manganiferous zone of the former occurrence is considerably regionally metamorphosed while the Newfoundland sediments show very little change in this way. According to the above analyses, assuming that the imported specimens are representative of the region concerned, the deposits are very different in as much as they consist mostly of rhodonite and manganiferous cherts while those of Newfoundland are carbonate-oxides and oxide-carbonates of manganese.

## VI. CHEMISTRY OF THE MANGANESE DEPOSITS.

The most striking feature of the accompanying analyses is the high content of MnO which ranges from 19.42 per cent. in **Analysis J**, to 49.25 per cent. in **Analysis D**, with an average content of 30.02 per cent and an average metallic manganese content of 24.64 per cent.

The manganese is present for the most part as the carbonate,  $\text{MnCO}_3$  or rhodochrosite, which varies from 10.23 per cent. in the red band (**Anal. E**) to 44.39 per cent. in the green band (**Anal. A**) of the Manuels deposit. Rhodochrosite is not recognizable as such because of the impalpable fineness of grain of the deposit.

Solubility tests made of the red band (**Anal. E**) which has 27.61 per cent. of  $\text{SiO}_2$ , in which  $\text{HCl}$  was used as the solvent, show that the manganese must be present in some other combination than in that of the silicate, as the residue was about sufficient to cover the total silica,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ . In **Anal. D**, it is evident that the two most important constituents are  $\text{MnCO}_3$  and  $\text{MnO}_2$  with percentages of 32.89 and 28.93 respectively and that the excess manganese calculated as the oxide is more than sufficient to form an important manganese silicate as the mineral percentage of  $\text{SiO}_2$  is only 5.40, which fact lends support to the result of the solubility test made with the red band, **Anal. E**. A similar interpretation might be made with the Topsail ore (**Anal. I**) which is primarily an oxide ore with  $\text{MnO}_2$ —34.25 and  $\text{MnCO}_3$ —11.27.  $\text{SiO}_2$ , of which there is 10.32 per cent., probably is present in an uncombined state. The comparative instability of  $\text{MnCO}_3$  would, however, lead one to suspect that the excess  $\text{MnO}_2$ , where not of primary origin, was a derivative of the carbonate and not combined with  $\text{SiO}_2$  to form the silicate,  $\text{MnSiO}_3$ .

ANALYSES OF MANGANESE DEPOSITS OF NEWFOUNDLAND AND ELBINGERODE.

	$\text{SiO}_2$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{Al}_2\text{O}_3$	$\text{MnO}$	$\text{CaO}$	$\text{MgO}$	$\text{BaSO}_4$	$\text{P}_2\text{O}_5$	$\text{H}_2\text{O}$	$\text{CO}_2$	Total
Manuels:												
A, Green band	7.24	3.36	3.21	6.11	35.53	11.30	2.30	....	....	2.98	28.06	100.09
B, Pink nod. . .	5.14	1.40	....	1.64	20.49	32.92	.01	....	....	1.65	36.77	100.02
C, Green nod. . .	10.31	7.35	....	3.68	31.76	10.47	1.80	6.43	....	2.85	25.31	99.96
D, Brown band	10.23	1.32	.89	4.14	49.25	8.11	3.02	....	....	1.31	21.83	100.10
E, Red band . .	27.61	4.25	1.69	6.96	26.05	9.94	3.49	....	4.71	4.73	10.57	100.00
F, 219 A 11 . . .	18.42	6.33	....	7.95	21.44	14.46	5.01	....	3.46	2.58	21.20	100.85
G,* 219 A 3 . . .	58.62	3.12	3.66	22.42	.43	1.25	.26	....	....	.54	3.99	94.29
H, 219 A 13 . . .	25.20	10.13	....	7.67	....	23.50	4.78	....	17.68	2.71	2.23	93.90
Topsail:												
I, 219 E 4 . . . .	18.04	4.82	....	6.58	41.26	2.24	2.39	5.40	....	7.98	8.34	97.05
J, 219 E 6 . . . .	18.24	10.01	....	14.52	19.42	13.74	4.94	....	1.71	2.07	24.01	99.66
K, Smith Pt. . .	15.14	9.22	....	12.04	25.63	10.04	3.72	....	1.26	2.73	21.05	100.83
Elbingerode:												
L, Elbin. (—) . .	39.10	1.87	....	10.79	27.69	1.00	6.08	....	....	1.13	13.13	100.79
M, Elbin. (+) . .	76.40	.007	....	2.46	10.53	1.62	1.81	....	....	.80	7.32	100.94
N, Elbin. (=) . .	7.10	.62	....	.76	52.01	2.26	1.17	....	....	1.70	32.20	97.82

\* Analyst, Mr. A. F. Buddington.

The evolution of  $\text{Cl}$  during the digestion of the samples with  $\text{HCl}$  is evidence that the excess  $\text{Mn}$  occurs as some peroxide. As



there is considerable water in the Topsail ore (*Anal. I*), the excess manganese probably is present as a hydrated peroxide such as psilomelane but probably in a very fine state of dissemination. The remarkable feature of the samples studied is the conspicuous absence of the dark oxides of manganese so far as macroscopic and microscopic observations are concerned but the reason for this may be, in the case of the lighter samples, anyway, that where there are abundant hematitic spherules there may be some masking. With the darker specimens studied, such as the red and brown bands at Manuels and the baritic manganese ore of Topsails (Figs. 22 and 32), the conspicuous manganiferous and ferruginous staining might easily mask finely disseminated particles of the peroxide of manganese.

RECALCULATED ANALYSES.

	MnCO <sub>3</sub> .	MnSiO <sub>3</sub> .	MnO <sub>2</sub> .	CaCO <sub>3</sub> .	MgCO <sub>3</sub> .	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .	SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	BaSO <sub>4</sub> .	H <sub>2</sub> O.	Clay.	Total.
RA.....	44.39	.....	8.08	20.11	4.21	.....	.....	3.36	.....	.86	18.24	99.2
RB.....	29.32	.....	2.34	58.05	29.32	.....	3.78	1.40	.....	1.06	4.07	100.02
RC.....	39.56	.....	7.30	18.61	3.79	.....	5.94	7.35	6.29	1.51	9.17	99.52
RD.....	32.89	.....	28.93	14.01	5.90	.....	5.40	1.27	.....	.72	11.08	100.20
RE.....	10.23	.....	19.71	7.50	7.25	10.31	19.44	4.25	.....	1.87	19.01	99.57
RF.....	19.22	.....	9.36	18.61	10.54	7.50	9.18	6.22	.....	.....	19.61	100.24
RG.....												
RH.....	.....	.....	.....	4.70	9.19	38.77	16.20	10.06	.....	.....	19.11	98.03
RI.....	11.27	.....	34.25	4.00	4.97	.....	10.32	4.82	5.40	5.41	16.30	96.74
RJ.....	16.79	.....	.....	20.91	10.37	3.75	1.20	10.01	.....	.....	36.38	99.41
RK.....	26.91	.....	9.00	15.21	7.75	2.50	.84	9.22	.....	.....	30.06	101.49

ELBINGERODE

RL.....	15.05	33.98	.....	1.70	12.64	.....	10.97	1.75	.....	.....	23.76	99.85
RM.....	10.00	8.00	.....	2.80	3.79	.....	69.84	.....	.....	.....	6.11	100.54
RN.....	76.13	8.92	.....	4.00	2.44	.....	2.16	.37	.....	.....	5.98	100.

The two most conspicuous mineral associations of the manganese deposits of southeastern Newfoundland are the tricalcium phosphate, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, and barite, BaSO<sub>4</sub>. Only a few of the beds were analyzed for the former of these constituents where percentages of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> ranged from 2.50 at Smith Point (*Anal. K*) to 10.31 (*Anal. E*) at Manuels. *Anal. H* shows 38.77 per cent. of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, references to which are made on pages 409 and 453. It

is quite probable that others of the manganiferous beds analysed are phosphatic.

Barite ( $\text{BaSO}_4$ ) is probably more common than the analyses indicate and is probably included with the  $\text{SiO}_2$  and  $\text{CaO}$ . It is a conspicuous associate of these deposits, as has been found to be the case with manganese deposits in other parts of the world. The chemical reason for this association of two very different chemically-acting elements, as well as the genesis of barite are discussed on pages 451-453.

$\text{Al}_2\text{O}_3$ , though not as abundant in the important manganiferous beds as in a typical shale, which that of **Anal. G** approximates, is of sufficient abundance to connect these deposits with the argillaceous sediments.  $\text{CaO}$  and  $\text{MgO}$  are in greater amounts than in ordinary shales, giving the deposits a calcareous or dolomitic character.

From a study of the mineral percentage composition of the samples analysed, the manganese rocks are found to be essentially calcareous or dolomitic argillaceous carbonates and oxides or carbonate-oxides of manganese, with hematite, barite, and tri-calcium phosphate as the chief accessories.

The following iron determinations of the green and red shales of the manganese zone at Manuels, Conception Bay, show some interesting results.

	FeO.	Fe <sub>2</sub> O <sub>3</sub> .
Red shale, 210 A 4 .....	4.58	3.86
Green shale, 219 A 3 .....	3.66	3.12
Red band, 219 A 7 .....	1.69	4.25
Green band, 219 A 7 .....	3.21	3.36

It is quite evident from the above analyses that the color in the green shale A 3 and in the green band A 7 is not due entirely to the ferrous iron as we find considerable  $\text{Fe}_2\text{O}_3$  in both. In the green shale, A 3, there is an excess of .54 per cent. of  $\text{FeO}$  over the  $\text{Fe}_2\text{O}_3$ , while in the green band, which is manganiferous, there is an excess of .15 per cent. of the ferric oxide (hematite) over the ferrous oxide. In the green band we should expect a masking of the green by hematite inasmuch as there is such an excess of the ferric over the ferrous. Thin sections of this band and the green shale reveal some hematite but in very inconsiderable amounts; not enough, at

all events, to explain the percentages as brought out in the analyses. It would seem then that the ferric iron does not exist essentially as hematite but as a silicate or some other allied mineral, and that the green color so predominant in the manganese bands and shales may be due to the ferrous and ferric silicate.

The presence of hematite in the red band has undoubtedly caused the red coloration and the same may be said in reference to the red shale, 210 A 4, where there is an excess of .72 of FeO over the  $\text{Fe}_2\text{O}_3$ , but in these there undoubtedly has been sufficient masking of the ferrous and ferric silicates of iron by the hematite.

The production of the hematite was probably brought about by the conversion of the silicate into  $\text{Fe}_2\text{O}_3$  through oxidation.

#### VII. GENESIS OF THE MANGANESE DEPOSITS AND ASSOCIATED MINERALS.

So many of the sedimentary manganese deposits described in the literature are in such a highly altered condition because of oxidation and deeper seated metamorphic influences whereby the original or primary manganese minerals have been so altered as to be of little genetic significance, that the carbonate-oxide manganese ores of southeast Newfoundland, which are surely primary ores, give promise of yielding evidence of considerable value on the question of genesis. In considering the genesis of any marine sedimentary manganese deposits, we are, however, confronted with many grave difficulties because we are dealing with submarine chemical conditions of which little is known and with diagenetic processes of which still less is known. It is also very difficult to advance any suitable chemical hypothesis founded upon some reaction that successfully works out in the laboratory which will not be of doubtful application in nature. With these difficulties in mind the following subjects relating to the genesis of the manganese deposits of southeast Newfoundland will be considered: Early Cambrian physiography; Nature of deposited sediments; Conditions under which the manganese deposits were formed; Summary of genesis of manganese; Diagenetic structures, as banded, nodular and oölitic; Genesis of barite; Genesis of tricalcium phosphate; Association and separation of iron.

EARLY CAMBRIAN PHYSIOGRAPHY.—In all probability the area occupied by Trinity, Conception, Placentia, and St. Marys Bays, the included land and the western and eastern margins including the present known Cambrian outcrops, was a continuous body of water shortly after the beginning of the Cambrian transgression. West and east of this Cambrian sea were high and extensive pre-Cambrian land areas. The great crustal movements which threw the pre-Cambrian into mountain ranges probably converted the portion now occupied by the four bays and adjacent land into a narrow basin. The main topographic features of the southeastern part of Newfoundland during the beginning of the Cambrian were two land areas of great relief separated by a comparatively narrow trough which had a general north-south direction.

Whether this trough was a closed one or not, it would be difficult to prove, but from the requirements of the problem it is necessary to postulate a more or less closed basin or coastal shoals or lagoons. Concentration of manganiferous soluble salts could go on satisfactorily only in a more or less restricted shallow sea where the water was comparatively quiet. The facts that ripple marks occur occasionally in the deposits such as at Manuels and that a shallow water fauna abounds such as trilobites are sufficient indication that there was a shallow sea at this time.

NATURE OF DEPOSITED SEDIMENTS.—Into this trough during early Cambrian times great quantities of mud were brought by rivers draining the pre-Cambrian land masses and to a lesser extent by the action of the waves on the shore line. As has already been stated the greater thickness of shales in the western portion of the basin is due to the fact that sedimentation had been going on for a longer time in that part of the basin which was in all probability the deeper part. It is also quite possible that the western parts of this trough were receiving more sediments than the eastern. The shales are characterized by their predominant red color in the western parts of the basin interbedded with shales of green color and throughout the entire area by a highly manganiferous zone.

GENESIS OF THE MANGANESE ORE.—The distinctly bedded character of the manganese deposits and their occurrence in definite horizons of limited thickness and considerable horizontal range seem



to point clearly to the conclusion that the deposits are essentially of sedimentary origin, rather than products of a later ground water or weathering concentration. But beyond this conclusion, there is room for great diversity of opinion.

Two questions present themselves at the outset of the inquiry: Was the manganese deposited contemporaneously with the clastic sediments in its present degree of concentration? Or, was it somewhat disseminated through the muds and subsequently concentrated by diagenetic agents? While the first of these alternatives is held by the writer to be highly probable, no positive and final answer can be given to these and to many other questions raised by a study of the problem of genesis, although various suggestions are presented in the following pages.

Manganese exists in sea-water and has been noted by Forchhammer and by Dieulafait (6: 718) but not in sufficiently concentrated form to produce deposits similar to those under consideration. Murray and Irvine (19: 735) found that the red muds of the mid-Pacific and Indian Oceans, which were made up in large parts of basic vitreous volcanic minerals, were responsible for the large amounts of pulverulent and nodular ferromanganese. These nodules consist on the average of 29 per cent. of  $\text{MnO}_2$  and 21 per cent. of  $\text{Fe}_2\text{O}_3$  with the remainder largely clayey material. The basic glasses contain the only important primary manganese-bearing minerals in the ocean and the manganese is reported by Murray and Irvine to have undergone conversion into the soluble bicarbonate which upon reaching oxygenated surface waters, is decomposed with precipitation of the dioxide. The particles of  $\text{MnO}_2$  falling to the bottom gather upon various objects which serve as nuclei for concretions, or the nuclei themselves may have been the cause for the precipitation. Murray and Hjort (17: 192) in this connection say:

"It should be noted that these oxides need by no means necessarily assume a concretionary form. They are very commonly found as thin incrustations on granular and fragmentary objects. Furthermore many, if not most, of the pelagic clays contain intimate admixtures of finely divided brown manganese and occasionally of limonitic iron. Here the supersaturation would seem to have been so high as to transgress the metastable limit, whereupon the oxides have precipitated themselves without the intervention of nuclei; they certainly must have been precipitated from solution."

According to Leigh Fermor (8: 403) the origin of the deep-sea nodules is summed up as follows:

"1. The manganese, although probably partly derived from cosmic dust and volcanic débris, has been mostly precipitated from solution in the sea water, the manganese salts having been originally brought into the sea by rivers.

"2. The manganese oxide, although possibly partly precipitated as a result of the action of the vital processes of organisms, both vegetable and animal, has been mainly precipitated by calcium carbonate aided by the obscure process of segregation from solution round a nucleus.

"3. Where the sea-bottom consists largely of calcareous sediments, the precipitation may have been mainly brought about by the solution of some of this calcium carbonate with the deposition of an equivalent amount of manganese oxide owing to the presence of free oxygen.

"4. Where the sea-bottom consists of red clay, it does so because the depths are there so great that the tests of thin-shelled organisms are completely dissolved by the sea-water before they reach the bottom. The calcareous matter in being dissolved deposits an equivalent amount of manganese oxide, which descends to the bottom, and there acts as a nucleus for the segregative extraction of manganese from the waters at the sea-bottom. The deposition of manganese oxide by means of calcium carbonate associated with the red clays probably also occurs to a subordinate extent, for the shells of thick-shelled organisms may reach the bottom before being entirely dissolved."

This summary of Fermor's is quoted in full here because of the marked divergence of his views from those of Murray and Irvine, and because of the greater stress laid upon Penrose's idea of the precipitation of manganese oxide by calcium carbonate.

It is the belief of the writer that the early Cambrian Sea of south-eastern Newfoundland must have had so restricted and shallow a character as to allow of a concentration of the manganese salts sufficient to form deposits of such dimensions and character as we now find. Whether the manganese was brought down entirely in solution or only partially so, or entirely or partly in mineral combination as fine muds from which the manganese was subsequently dissolved, one cannot say at present. Both muds and solutions probably have contributed the manganese which forms in great part the deposits as we now find them.

The conditions which brought about the formation of the carbonate and oxide of manganese are problematical. It is generally

supposed that manganese exists in solution as a bicarbonate or a sulphate. In their work on the Blue Muds of the Clyde Sea area, Murray and Irvine (19: 728) found that the bicarbonate of manganese was derived "first from the direct decomposition of the rock fragments in the mud by the alkaline carbonates in the sea water or, second, from the reduction of the higher oxides of manganese by the organic matter in the muds." In many respects the Clyde Sea area of England is similar to what the lower Cambrian sea of Newfoundland must have been. It receives detritus and waters draining lands which are in large part of an igneous and sedimentary character (19: 780).

"What is known as the Clyde Sea Area consists of a series of submarine basins, separated from each other by submarine barriers. The depth of the basins ranges from 30 to 106 fathoms, and the depth of water over the intervening ridges varies from 3 to 15 fathoms. In all the deeper parts of the basins there is a bluish mud, in which, as a rule, no manganese nodules are found, but on the immediate surface of the deposit of Blue Mud there is a surface layer with a reddish or light gray color, in which deposits of manganese dioxide occur. When stones are dredged from these muds many of them are surrounded by a dark ring of manganese dioxide, marking the depth to which they have been embedded in the mud. The whole upper surface of the stones has likewise a slight coating of manganese, while a portion imbedded in the mud is free from these manganese deposits."

He goes on to say that

"The formation of manganese nodules on the immediate surface of the deposit, on the tops of the barriers, and in the pit-like depressions, is most probably to be accounted for by the more abundant supply of oxygen, or the diminished amount of decomposing organic matter in these positions."

A somewhat similar set of conditions probably was present in the muds and superjacent sea water of the Cambrian basin of Newfoundland with the exception that instead of all the bicarbonate being converted into the dioxide the greater proportion of it was precipitated as the carbonate of manganese ( $\text{MnCO}_3$ ). The liberation of  $\text{CO}_2$  from the bicarbonate of calcium in solution has been experimentally effected by evaporation, increasing the temperature, or through agitation of the solution. It would seem to the writer that the liberation of the  $\text{CO}_2$  from the manganese, calcium and magnesium bicarbonates might have taken place through evapora-

tion resulting in a contemporaneous formation of manganese, calcium and magnesium carbonate. As the analyses show from 1.25 to 32.92 per cent. of  $\text{CaCO}_3$  and from .01 to 5.01 per cent. of  $\text{MgCO}_3$  this would seem to support such an action.

There is a possibility that the decomposing organic matter present in the muds might have caused a deoxidation of the sulphates of the sea-water and of  $\text{MnO}_2$  with the subsequent formation of  $\text{FeS}_2$  and  $\text{MnS}_2$ . The latter, being very unstable, would pass immediately into the bicarbonate to be subsequently freed of its  $\text{CO}_2$  to form the carbonate and if oxidized would pass into the dioxide. Such a process might account for the carbonates and oxides of manganese and the little pyrite that occurs. Though there is evidence of life in the manganese deposits of Newfoundland as furnished by the fossil trilobites, pteropods and phosphatic accumulations, we have no evidence that there was any great abundance. However these deposits resemble the Blue Mud studied by Dittmar (6: 43) which are a variety of terrigenous deposit which

"covers about 15,000,000 square miles of the sea bed, and is chiefly found in estuaries, harbours, enclosed seas, and along continental coasts where rivers pour their detrital matter into the ocean."

According to the "Challenger researches" there is an abundant fauna on these muds, which feeds chiefly on the organic remains that fall from surface waters. If any analogy can be made between the ancient terrigenous deposits and the more modern ones such a chemical action as described above might very well have taken place.

If the muds on the bottom of the basin contained considerable quantities of decomposing organic matter, conditions would favor a reduction of the higher oxides of manganese, the evolution of much  $\text{CO}_2$  and the consequent formation of the bicarbonate of manganese. The subsequent liberation of the excess  $\text{CO}_2$  from the bicarbonate to form the carbonate and, where oxidizing influences are active, the oxidation of this carbonate would complete a series of reactions capable of forming the manganese deposits with which we are dealing. It is very probable that these muds contained considerable quantities of decomposing organic matter and were evol-



ing considerable  $\text{CO}_2$ . According to the "Challenger researches," when a large quantity of carbonic acid was found in oceanic waters it was "at the bottom over Blue Muds." The great difficulty in this series of reactions is to find in nature the conditions which will bring about the liberation of the excess  $\text{CO}_2$  from the bicarbonate to form the carbonate, such as evaporation, increase of temperature, or agitation. If quiet waters are postulated for the formation of manganese carbonate it is quite conceivable that either of the conditions such as evaporation or an increase of temperature might easily be obtained particularly in shoal waters. It is very doubtful, however, in the case of agitated waters whether laboratory conditions can be simulated in nature, because of oxidizing influences whereby some oxide of manganese would form more readily than a carbonate. After the carbonate had formed there would be no particular difficulty in conditions being present which would bring about the oxidation of the carbonate because of the presence of oxygen. The excess oxide of manganese found in the Newfoundland deposit may in part have originated in this way.

Penrose (20: 563) suggested that "carbonate of lime on the sea floor may have acted as a precipitating agent" or as it passes through the sea-waters in the form of organic remains or mineral particles a substitution takes place whereby a solution of the calcium carbonate with a corresponding precipitation of manganese occurs. Fermor develops this suggestion in his explanation of the origin of the deep sea nodules as quoted on page 444. Such an explanation might apply to the origin of the primary oxides of the Newfoundland deposits.

It is possible that manganese may have been present in the sea-water as a chloride. L. De Launay (5: 533) says that "manganese chloride with sodium bicarbonate produces manganese carbonate."

When we stop to consider that manganese only averages .07 per cent. of the lithosphere (Clark, 2: 32) and is 70 times less abundant than iron which averages 4.43 per cent. and compare with these figures the percentage of manganese in the deposits under consideration which is 24.64 we can obtain some idea of the enormous concentration there has been in the production of these deposits.

We have discussed the nature of the sediments and learned that these terrigenous deposits must have been derived from the pre-Cambrian land masses which existed in far greater extent on the east and west of the Cambrian sea than the present areas outlined on page 373. The interbedded character of the manganiferous and argillaceous layers signify alternating conditions of chemical precipitation and mechanical deposition, there being, during the formation of the deposits, times when the Cambrian sea was more manganiferous with conditions such that precipitation of manganese carbonate and the oxide was the relatively important feature while, at other times, mechanical deposition of fine muds was the rule. It is more than likely that the greatest portion of the manganese was contributed to the sea in the form of the dissolved bicarbonate by the streams which transported the clastic sediments and that these sediments were not themselves responsible for the major contribution, though undoubtedly the manganese minerals in the muds underwent some solution both during their transit to the sea bottom and during diagenesis. The streams which were responsible for the transportation of the sediments of the manganese deposits and also held, as chief contributors of the manganese, drained the pre-Cambrian land areas above referred to. A modern river like the Ottawa which drains a pre-Cambrian area consisting in great part of Laurentian and Huronian rocks and in all probability not very different from the pre-Cambrian rivers of ancient Newfoundland, has .86 parts per million of manganese in its waters according to an analysis made in 1907 (Shutt, 22: 175).

Manganese in river water results from the solution of manganiferous silicates such as pyroxene, olivine, micas, amphiboles, epidotes and chlorites, some of which are the common and essential basic rock-forming minerals of any igneous and metamorphic pre-Cambrian area. On the decomposition of these elements the manganese is converted into carbonate or oxide and enters into solution, when conditions are favorable, as the bicarbonate, in which form it is carried to the sea, unless oxidized in transit, there to await the further changes into the oxides,  $\text{MnO}_2$  and  $\text{Mn}_2\text{O}_3$ , or the carbonate,  $\text{MnCO}_3$ , depending upon the conditions suggested in the preceding pages. Analyses of some of the pre-Cambrian rocks in the vicinity

of Conception and Trinity Bays may be of interest at this point as illustrating the manganese content of some of the rocks which are most like those existing during the formation of the deposits:

	MnO.
Monzonite, Woodford .....	.19
Quartz porphyry, Manuels .....	.11
Conception sl., Random Is. ....	.12
Granite, Manuels .....	.13
Aporhyolite, Manuels .....	.12
Basalt, Blue Hills .....	.48
Analyst, A. F. Buddington.	

Similar analyses have been made from the rocks of the Clyde pre-Cambrian drainage area and show from .1 to .7 of a per cent. of MnO (Murray and Irvine, 19: 722). In all probability then the pre-Cambrian rocks on the east and west of the Cambrian basin were the ultimate source of the manganese.

#### SUMMARY OF GENESIS OF MANGANESE.

*Ultimate Source* of the manganese was the manganese-bearing silicates of pre-Cambrian igneous and metamorphic rocks east and west of the Cambrian Sea.

*Solution* of manganese-bearing silicates and conversion of the manganese into the soluble bicarbonate; under favorable conditions oxides of manganese resulted from the oxidation of the bicarbonate of manganese.

*Transportation* of the manganese chiefly as the bicarbonate and to a less extent as suspended particles of oxides by pre-Cambrian drainage systems to Cambrian basins.

*Concentration* of the salts of manganese chiefly as the bicarbonate in the sea-water immediately overlying the deposited muds.

*Precipitation* of manganese carbonate from solution through liberation of CO<sub>2</sub> from the bicarbonate, or of the oxide.

*Clastic Origin of Some Manganese.*—While the main contribution of the manganese came from the pre-Cambrian drainage area in solution undoubtedly the deposited muds supplied a minor portion.

## DIAGENETIC STRUCTURES

BANDED STRUCTURES.—By referring to the description of layer 219 A 7 we see that it is a red manganiferous shale with green and brown jaspery bands which may be rather uniform in thickness and may alternate with each other. The green band predominates over the brown so that the greater alternations occur with the green and red bands. Throughout the red shale are numerous nodules of the green and brown jaspery carbonate-oxides of manganese and within the bands themselves are nodular and concretionary forms. The alternating banded and concretionary forms within this bed would indicate alternating conditions of precipitation followed by diagenetic segregational processes which resulted in the formation of nodules and lenticles. Very thin and interrupted laminae of the red band are found with the green bands. The green and brown bands often occur intergrown with each other. From these observations it would seem that these banded structures were evidence of alternate periods of precipitation and that they have assumed their present indurated and concretionary nature by segregational processes which were active throughout the diagenesis of the bed.

NODULES.—One of the most characteristic features of the shales of the Lower Cambrian is the great prevalence of the nodules (Figs. 14 and 15). The following suggestion is offered as to the origin of the form of these nodules with the hope that this line of investigation may be taken up in greater detail at some future time. Though various theories have been suggested for the origin of oölitic spherules and nodules, in general, along organic and inorganic lines, nothing of a very definite nature has been brought out as to the origin of their form. The suggestion that surface tension may be the cause of this form is here made. This peculiar and prevalent nodular character of certain beds was brought about in all probability by the tendency of surface tension to decrease the surface during the diagenetic stage. Solutions carrying manganese filtering through muds or nearly consolidated muds or shales would quite naturally under certain chemical and physical conditions have the tendency to decrease the surface tension at the contact of the three physical phases; liquid, colloid, and solid. Starting with a



mineral particle such as rhodochrosite or calcite as a nucleus, with the formation of the nodule, there will be a decrease in the concentration of the solution at the contact with the nodule which will be accompanied by a reduction of surface tension. If we are dealing with a liquid-liquid phase we would have a spherical nodule in which case both liquids would be easily deformable and the surface would tend to become a minimum. Our twofold phase, liquid-solid, or threefold phase including the colloidal phase which probably plays a part, only allows of deformability on the part of the liquid and partial deformability on the part of the nodule. Under the bedded conditions of this two or three fold solution, colloid and solid phase the tendency of the surface tension to reduce the surface to a minimum is well exemplified in the discoidal nodule.

**SPHERULES.**—One of the characteristic features of this deposit is the occurrence of hematite in spherule-like forms and larger, roughly spherical aggregates. Fig. 26 illustrates the occurrence. They differ decidedly from the spherules of the Wabana, Clinton, and other typical oölitic iron ores in that they are less symmetrical and are without any visible nuclei. These spherules are here described as incipient in as much as they seem to lack full development or to have been impeded in their growth. Such a retardation of development might have arisen from their growth in clayey sediments which were still unconsolidated.

**MINERAL ASSOCIATIONS.**—The three important mineral associations of the manganese deposits of S. E. Newfoundland are barite, tri-calcium phosphate and hematite which will now be considered with reference to their occurrence, association and genesis.

**BARITE.**—Barite is one of the most characteristic mineral associations of the deposits under consideration as is often the case with manganese deposits elsewhere in the world. It is particularly characteristic of the Manuels, Topsail and Smith Point localities and occurs in various ways.

Barite is found in small veins crossing a cryptozoan nodule showing quite clearly its epigenetic character so far as that particular portion of the bed is concerned. Fig. 23 (Slide 276) shows a solitary crystal fragment of barite in a carbonate-oxide of man-

ganese groundmass showing possibly a diagenetic replacement. Barite also occurs as disseminated anhedral crystal grains or blades in the cores and outer zones of nodules at Manuels, which is very suggestive of diagenetic processes (Fig. 16, Slide 288). At Topsail (Fig. 31, Slide 269) barite occurs as bundles of blades or sheath-like aggregates in a manganese oxide groundmass strongly suggesting replacement.

In other parts of the world barium is often found replacing manganese in psilomelane and sometimes enters largely into the composition of wad, specimens from Romanèche containing as much as 16.2 per cent. of BaO (Dana, 3: 258). A very striking phenomenon shown by the barite is its replacement by chlorite (Fig. 12, Slide 296, and Fig. 34, Slide 272).

Just why there is this common association of two very unlike elements we have no definite information. De Launay (4: 52) gives the following explanation for epigenetic deposits:

“The association between barite and manganese though very frequently exhibited in surface formations, in many cases these two substances are being concentrated by circulating waters in pockets or fissures of terranes.”

Various conditions may produce barite with barium salts in solution but only one seems to apply to the occurrences under consideration. As there are evidences of diagenetically and epigenetically formed barite in the deposits, it is quite possible that there has been an intermingling of solutions carrying barium carbonate and some sulphate resulting in the formation of barite. According to De Launay (4: 52)

“Barite being remarkably insoluble is one of those barium compounds which not only has the propensity to segregate and all at once to be transformed into the carbonate but also the tendency under the influence of  $H_2SO_4$  produced by the superficial oxidation of the metallic sulphides to pass into the state of barite.”

The replacement of the colorless barite by the pale green chlorite begins about the edges and along cleavage cracks of the former. The chlorite gradually spreads while the intervening portions of barite decrease until wholly eliminated, resulting in a pseudomorph of chlorite after barite. In general appearance of its various stages,

the process is quite like the serpentinization of olivine but differs essentially from the latter alteration in the fact that the secondary mineral, chlorite, derives none of its material from the original mineral, barite, its change involving a complete replacement by wholly new material. It is a marked example of the comparative ease with which substances which, like barium sulphate are regarded in the laboratory as very stable, yield to the attack of natural reagents.

This replacement seems to have accompanied a more or less general chloritization of the whole formation, at a period long subsequent to the concentration of the manganese ore and under totally different conditions.

PHOSPHATE.—Tri-calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$  also is a very conspicuous accessory of the manganese deposits of Newfoundland, averaging, for those beds of which analyses were made, about 6.0 per cent. and for the phosphatic nodules of the nodular bed overlying the manganese zone at Manuels, 38.77 per cent. When we stop to consider the amount of phosphorus in the lithosphere as .11 per cent. (Clark, 2: 32) the amount of concentration in these deposits, particularly in the nodules, becomes very noticeable and something of great interest. The similarity in chemical composition of the phosphatic nodules of Manuels brook and those of Hanford brook, N. B., has been referred to on page 409. As the writer has been unable to make as thorough a study of these nodules as he would have liked, it is hoped that at some future time the investigation may be continued. At this time then a very brief resumé of the modes of concentration of phosphorus may be of interest because of apparent application to the deposit under consideration.

According to De Launay (5: 646) there are three stages in the concentration of phosphatic deposits, namely solution of calcium phosphate, in which he considers that in surface conditions

“the constant presence of carbonic acid and sodium chloride or chlorhydrate of ammonia in the waters determines the solution of phosphate.”

The second stage is that in which organisms play an important rôle.

"The faculty which live organisms have of throwing into very dilute solutions those substances which to them are necessary and of making them undergo a primary stage of concentration has played a great rôle for the phosphates." De Launay (5: 646).

The third stage called by De Launay, "*Remises en mouvement*" consists in a dissolution of the phosphate contained in preceding deposits which is followed by a reprecipitation of the same upon anything which has served as a center of attraction. The tendency in this mode of concentration is for the phosphate to become more and more like the original apatite in composition, the ultimate source of the phosphorus. It involves both a chemical and a mechanical action, the former in dissolution and reprecipitation and the latter in the formation of nodules which, according to the suggestion of the writer in connection with the manganese nodules of Manuels, may be of physical nature, namely the result of surface tension.

IRON.—An interesting, and yet problematical, point arises here in connection with the association and separation of iron and manganese as related to the manganese deposit under consideration. We should expect, in as much as both elements are taken into solution, that they both might be precipitated together as is sometimes the case with bog ores or, if separated, at no great stratigraphic distance. Because of their different rates of oxidation and different degrees of solubility, however, a separation is effected. Assuming both elements entering into solution contemporaneously, the iron would oxidize first, precipitating as  $\text{Fe}_2\text{O}_3$ , while the manganese, remaining in solution longer, is precipitated either as  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$  or  $\text{MnCO}_3$ . Though the Newfoundland manganese deposits contain iron, it is much less in proportion to what it would be if both were precipitated together (see Analyses, p. 438) considering the relative abundance of the two elements in the lithosphere referred to on page 447.

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